

**GEOCHRONOLOGY OF ROCK SYSTEMS**

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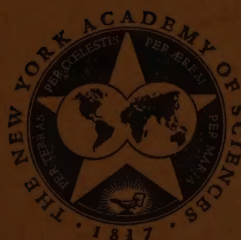
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CONTENTS

Preface. By RHODES W. FAIRBRIDGE.....	163
Introductory Remarks. By J. LAURENCE KULP.....	165

Part I. Methodology

Present Status of the Decay Constants. By L. E. GLENDENIN.....	166
The Rubidium-Strontium Method. By P. W. GAST.....	181
Metamorphic Chronology by the Rubidium-Strontium Method. By W. COMPSTON AND P. M. JEFFERY.....	185
Mineral Ages and Metamorphism. By STANLEY R. HART.....	192
Graphical Interpretation of Discordant Age Measurements on Metamorphic Rocks. By L. O. NICOLAYSEN.....	198
Analyses of Identical Samples by More Than One Laboratory. By LEONARD F. HERZOG.....	207
The Potassium-Argon Method: The Problem of Potassium Analysis. By WILLIAM H. PINSON, JR.....	221
The Base-Exchange Effects on Potassium-Argon and Rubidium-Strontium Isotopic Ages. By J. LAURENCE KULP AND W. H. BASSETT.....	225
The Retentivity of Radiogenic Argon in Ground Micas. By E. K. GERLING, I. M. MOROZOVA, V. V. KURBATOV.....	227
Radiogenic Argon in Minerals and Its Migration. By K. I. AMIRKHANOFF, S. B. BRANDT, E. N. BARTNITSKY.....	235
Summary of Discussion of Discordant Zircon Ages. By G. R. TILTON.....	276
Uranium-Lead Method on Zircons. By L. T. SILVER AND SARAH DEUTSCH.....	279
The Age of the Taraksky Granite Massif and Other Formations of the Yenisey Ridge. By K. K. ZHIROV, Yu. M. ARTYOMOV, M. I. VOLOBUYEV, V. V. ZHIROVA, K. G. KNORRE, L. M. KRIZHANSKY, Yu. Z. MOCHALOV, V. Ye. TIKHONOV.....	284

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## Part II. Dating Sedimentary Rocks

Glauconite as a Possible Means of Measuring the Age of Sediments. By P. M. HURLEY.	294
Utilization of Glauconite in Absolute Dating. By N. I. POLEVAYA, G. A. MURINA, G. A. KAZAKOV.	298
Dating of Black Shales. By JAMES C. COBB.	311
Dating of Tertiary Volcanic Rocks by the Potassium-Argon Method. By O. A. SCHAEFER, R. W. STOENNER, W. A. BASSETT.	317
Potassium-Argon Dates on Basaltic Rocks. By G. P. ERICKSON AND J. LAURENCE KULP.	321
The Possibility of Utilizing the Absolute Age of Metamorphic and Fragmental Rocks in Paleogeography and Paleotectonics. By A. Ya. KRYLOV.	324

## Part III. The Phanerozoic Time Scale

The Phanerozoic Time Scale: Introduction. By J. LAURENCE KULP.	341
Critical Points in the Cenozoic. By G. H. CURTIS, D. E. SAVAGE, J. F. EVERNDEN.	342
Potassium-Argon Dates of Upper Cretaceous Ash Falls, Alberta, Canada. By R. E. FOLINSBEE, H. BAADSGAARD, J. LIPSON.	352
Some Critical Points of the Post-Cryptozoic Geological Time Scale. By M. M. RUBINSTEIN.	364
Some Paleozoic Dates in Maine, Western Europe, and Southern United States. By H. FAUL.	369
Some Points on the Geological Time Scale from Nova Scotia and New England. By W. H. PINSON, JR.	372
Some Critical Points for the Paleozoic Time Scale from the British Isles. By R. ST. J. LAMBERT AND A. A. MILLS.	378
Bentonites as Absolute Time-Stratigraphic Calibration Points. By JOHN A. S. ADAMS AND JOHN J. W. ROGERS.	390

## Part IV. The Age of the Basement Rocks of the World: North America

The Northern Appalachians. By P. M. HURLEY.	397
Isotopic Ages from Northern New Jersey and Southeastern New York. By LEON E. LONG.	400
Potassium-Argon Isotopic Ages on Micas from the Southern Appalachians. By J. LAURENCE KULP AND F. DONALD ECKELMANN.	408
Summary of Discussion of Pre-Cambrian Mineral Ages from the Appalachian Province. By G. R. TILTON, G. W. WETHERILL, G. L. DAVIS.	420
Summary of Discussion on Age Measurements on the Basement Rocks of Ohio. By MANUEL N. BASS.	421
Age Measurements on the Cutler Batholith, Ontario, Canada. By G. W. WETHERILL.	423
Summary of Discussion of Mineral Age Measurements in the Canadian Shield. By L. T. ALDRICH AND G. L. DAVIS.	430
Summary of Discussion of Age Investigations at Sudbury, Ontario, Canada. By H. W. FAIRBAIRN.	431
Summary of Discussion of Pre-Cambrian of Central Wisconsin. By MANUEL N. BASS.	432
Canadian Shield Age Program of the Geological Survey of Canada. By C. H. STOCKWELL AND R. K. WANLESS.	433
Summary of Discussion of Pre-Cambrian Geochronology of Minnesota and Adjacent Areas. By S. S. GOLDICH, A. O. NIER, H. BAADSGAARD, J. H. HOFFMAN, H. W. KRUEGER.	442
The Age of the Basement Rocks of the Colorado Plateau and Adjacent Areas. By PAUL E. DAMON AND BRUNO J. GILETTI.	443
Absolute Age of Pre-Cambrian Rocks in Wyoming and Montana. By B. J. GILETTI AND P. W. GAST.	454
Periods of Orogeny in the Western Cordillera. By J. LIPSON, R. E. FOLINSBEE, H. BAADSGAARD.	459

## Part V. The Age of the Basement Rocks of the World: Eurasia

The Basement Rocks of Scotland and Ireland. By B. J. GILETTI, R. ST. J. LAMBERT, S. MOORBATH.	464
Some Potassium-Argon Ages on Rocks from the Norwegian Basement. By J. LAURENCE KULP AND HENRICH NEUMANN.	469
Isotopic Composition of Finnish Galenas. By OLAVI KOUVO AND J. LAURENCE KULP.	476
The Pre-Cambrian Geochronology of the Baltic Shield. By A. A. POLKANOV AND E. K. GERLING.	492
The Geologic Age of Pre-Cambrian Rocks of the Ukrainian and Baltic Shields. By A. P. VINOGRADOV AND A. I. TUGARINOV.	500



<b>Part VI. The Age of the Basement Rocks of the World: Africa and Australia</b>	
Radioactive Ages from the Pre-Cambrian Rocks of Australia. By A. F. WILSON, W. COMPSTON, P. M. JEFFERY.....	514
Summary of Discussion of Geochronology of Proterozoic Granites in Northern Territory, Australia. By H. W. FAIRBAIRN.....	521
An Upper Limit to the Age of the Witwatersrand System. By A. L. HALES.....	524
Age of Basement Rocks in Eastern United Arab Republic and Northern Sudan. By MOHAMED A. GHEITH.....	530
Review of Geochronological Knowledge in Middle and Northern Africa. By L. CAHEN.....	535
Summary of Discussion of Stratigraphic and Tectonic Interpretation of Certain Age Measurements in Southern Africa. By L. O. NICOLAYSEN.....	568

<b>Part VII. The Age of the Basement Rocks of the World: Other Areas</b>	
The Basement of Central and South America, or, How Not to Date a Continent. By P. M. HURLEY.....	571
The Absolute Ages of East Antarctic Rocks. By I. Ye. STARIK, A. Ya. KRYLOV, M. G. RAVICH, Yu. I. SILIN.....	576

<b>Part VIII. Synthesis of Crustal History and Pre-Cambrian Time Scale</b>	
Crustal History and the Pre-Cambrian Time Scale. By G. J. WASSERBURG.....	583



## PREFACE

Rhodes W. Fairbridge

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The New York Academy of Sciences is dedicated to the advancement of scientific research and discovery; it is its purpose "to provide a forum for the presentation and discussion of scientific problems; to publish and distribute the results of research, and to interpret them for the promotion of the common welfare." In this publication I feel we are doing just that. Moreover two further publications of this sort are currently in the planning stage: *Solar Cycles, Climatic Change, and Related Geophysical Problems*, to be based on a conference scheduled for February 1961, and *The Origin of Ore Deposits*, on a conference scheduled for February 1962. It is appropriate that in the vigorous turmoil of near-anarchy that is the great metropolis of New York today that we are endeavoring now to bring system and precision to the great time factor in earth history.

Time, indeed, is the essential parameter of geology, the factor that distinguishes it from all other sciences except astronomy. The very slowness of geological time is such that it cannot as a rule be observed or measured in men's lifetimes, and its passage can be deduced only from the evidence of the geological record of progressively accumulated rocks.

Formerly the only way of establishing geological time was by means of an utterly simple deduction, the Law of the Order of Superposition, which states that in an undisturbed stratigraphic sequence, sediments found at the base of a pile are the oldest and those at the top are the youngest. A complex system of named periods, approximately one dozen, covers geological time, and these in turn are broken up into series and stages. It is entirely a comparative methodology in which the respective periods, series, and other such units are of quite unequal value or length. They are simply labels that have been attached by the discoverers to the particular sequences of rocks that appeared distinctive and worthy of characterization. The chance element of who found that sequence and where has become crystallized into a rather rigid system in which the principle of historical priority, or first authorship, is widely accepted.

From time to time scientists have rebelled against this tyrannical hierarchy of accidental or chance discovery; there was A. W. Grabau, for example, who attempted to make periods all of the same length. However, he was born too soon: there was no way of determining that the units he thought equal were indeed uniform. Now we question further the concept that there is any really strict cyclicity involved; that remains to be determined in the future of geochronology.

Today stratigraphers are generally content to use their period and other unit terms simply as convenient and accurate labels for particular rocks, or for particular times when rocks were laid down. The International Geological Congress has a regular standing subcommission on stratigraphic nomenclature, whose sole duty is to codify, internationalize, and regulate the application of



these most essential labels. It should be stressed that no mathematical parameter is implied by any stratigraphic unit name. That such a name does have a very accurate and precise significance is sometimes lost on those without knowledge of natural systems, for the units are measured in terms often unfamiliar to the mathematician.

However a revolutionary new measurement is now introduced by the isotope geochemist, to whom the general geologist should be most grateful. Thus far our stratigraphy has been essentially a chronicle. Now we can begin to study processes in terms of rate, measured in unit years or years  $\times 10^6$ . Carbon 14 analyses permit the determination of rates of contemporary sedimentation. Longer-lived isotopes will permit the measurement of major earth cycles, of geosyncline development, or orogenies, metamorphism, plutonism, and volcanism. The vistas are immensely thrilling as we stand on this threshold.

## INTRODUCTORY REMARKS

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The potential for absolute geochronology arrived with the discovery of radioactivity, but quantitative isotopic methods were not born until the work of Nier on the U-Pb method about 1940. In the last decade we have experienced exciting discoveries and exponentially increasing knowledge in new age methods, new and more powerful analytical techniques and with them a better understanding of the geochemical processes that may affect the isotopic geochronometers. It is really only within the past three or four years that enough information and experience have been amassed to attempt seriously to date the major events in earth history.

Although sessions in national meetings have been devoted to age determination and informal conferences have been held on certain aspects of these problems, such as the valuable Pennsylvania State University Conference at University Park, Pa. in 1956, no conference had been held that attempted to synthesize and evaluate the broader geological implications of these developments since this large new body of quantitative data had become available.

The comprehensive conference on the Geochronology of Rock Systems upon which this monograph is based was accordingly arranged. Without the participation of the majority of the serious investigators in this field little of substance could have been accomplished. Contributors to this publication include representatives from nearly all laboratories engaged in this area of research.

Three principal subjects were adopted for consideration in planning the conference that has resulted in this monograph: (1) some remaining problems in the methodology of the U-Pb, Rb-Sr, and K-Ar geochronometers; (2) the geological time scale; and (3) the history of the basement rocks of the continents. Of necessity other interesting and related subjects, such as the age of meteorites, the development of other geochronometers, and  $C^{14}$  dating had to be omitted. Most of these matters, however, have been covered in other recent publications.

## Part I. Methodology

### PRESENT STATUS OF THE DECAY CONSTANTS\*

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Inasmuch as this part of the monograph is concerned with methodology, most of what I shall have to say here will be concerned with a fairly recent development in the problem of determining decay constants by measurement of specific activity, namely, the use of liquid scintillation counting.

It is unnecessary to consume space with a review of the literature on previous determinations of the decay constants used in geochronology. This information has been competently supplied in the review by Aldrich and Wetherill (1958)<sup>1</sup> and in the critique of the decay constants of uranium isotopes by Fleming *et al.* (1952).<sup>2</sup> Therefore I shall review the highlights of what my associates and I have been trying to do at the Argonne National Laboratory† recently with regard to making more precise determinations of the decay constants of Rb<sup>87</sup> and K<sup>40</sup> by using the liquid scintillation method. I shall conclude by stating briefly what we intend to do in the way of decreasing the present uncertainty in the decay constants of U<sup>235</sup>, U<sup>238</sup>, and Th<sup>232</sup>. The constants for uranium and thorium are already known within perhaps 2 per cent certainty and any improvement will be difficult.

Let us begin with the alkali element decay constants. Previous measurements of the constants for beta decay of Rb<sup>87</sup> and K<sup>40</sup> have a spread of about 40 per cent. As is known, one of the chief difficulties in attempting to count beta emitters is that associated with the self-absorption and scattering effects encountered with solid sources. One way to eliminate this problem is to put the radioactive substance in a gaseous form, but this cannot always be done because of the chemistry of the element involved. Placing the radioactive element in a scintillating crystal such as thalliated sodium iodide might also be considered. Here again there are difficulties involved. For example, in some cases it is not possible to incorporate a sufficient quantity of the radioactive substance into the scintillating crystal. In the case of the alkali metals, of course, this technique can be used and, indeed, the radioactivities of rubidium and potassium have been examined in alkali iodide scintillating crystals. However, here the problem of accurate background determination arises. It is difficult to prepare blank crystals with identical response to background radiations, and the correction for background is therefore uncertain.

In view of these various difficulties the advantages of the liquid scintillation-counting technique become apparent. The problem of self-absorption and scattering is avoided since the radioactive source is dissolved directly in the detecting medium, that is, the liquid scintillator, and counted under conditions of 100 per cent or "4 $\pi$ " geometry. A further consideration is that, in com-

\* The work reported in this paper was supported in part by the United States Atomic Energy Commission, Washington, D.C.

† Colleagues involved in various aspects of the work reported here are K. F. Flynn, D. W. Engelkemeir, A. H. Jaffey, and L. J. LeRoux.



parison with other techniques, relatively large quantities of radioactive samples can be placed in the detector. Since we are dealing here with long-lived radionuclides of low specific activity (disintegration rate per unit weight), an obvious advantage is gained. Finally, background measurements can be made accurately and conveniently by adjusting the pulse-height output of the liquid scintillator with a suitable quenching agent such as ethanol until the response of the background solution to a standard source is identical with that of the sample solution.

Let us go on then to the liquid scintillation-counting technique and the determination of decay constants (or half lives). The principle involved really is quite simple. The execution of it may not be.

The radioactive element in the form of soluble compound is dissolved in the liquid scintillator that is the standard mixture, terphenyl-POPOP in toluene. In the case of the alkali elements we use the salt of octoic acid (2-ethyl hexanoic acid). For details of the preparation of this compound and the scintillator I refer you to our recent paper on Rb<sup>87</sup>.<sup>3</sup> Uranium and thorium (and many other elements) are conveniently extracted into the liquid scintillator using alkyl phosphate extracting agents. This is an interesting topic in itself but I must defer further discussion of it owing to lack of space.

Light pulses produced in the scintillator by beta (or alpha) emission are fed through an electronic apparatus consisting of a multiplier phototube, amplifier, pulse-height analyzer, and scaler. In the case of beta radioactivity, the particles are emitted over a wide energy spectrum and, since the pulse height from a scintillator is proportional to the particle energy, a spectrum of pulse heights is obtained extending to very low values. Unfortunately, the intrinsic "phototube noise" caused by thermionic emission of electrons from the photocathode gives rise to a large number of pulses in the very low energy region and, consequently, it is not possible to obtain meaningful counts in this region. To obviate this difficulty, the sample is counted integrally at various bias (pulse-height discriminator) settings on the analyzer above the point of encroaching phototube noise. A plot is then made of net integral counting rate (background and noise subtracted) versus pulse height, and the curve is extrapolated to zero-pulse height to obtain the total disintegration rate of the sample. In most cases the required extrapolation is in the range of 1 to 10 per cent and the error introduced thereby is small. Some examples of such integral-counting rate curves will be shown later. Phototube noise presents no problem in alpha counting since the alpha particles are monoenergetic and the pulse heights occur in a relatively narrow range well above the noise region.

Having measured the total radioactivity of the sample in the manner just described, we now need to determine the number of atoms of the radionuclide present. This is accomplished by conventional gravimetric or volumetric analytical methods. In the case of rubidium or potassium the procedure is to ignite and weigh as the sulfate.

The decay constant ( $\lambda$ ) is then calculated from the equation for radioactive decay  $A = \lambda N$  where  $A$  is the absolute activity (total disintegration rate) and  $N$  is the number of atoms of the radionuclide. The equation relating the half life ( $T_{1/2}$ ) to the decay constant is  $T_{1/2} = \ln 2/\lambda$ .

Let us proceed now with a description of the apparatus employed in this

work. FIGURE 1 is a diagram of the first liquid scintillation-counting apparatus used in our laboratory. We have a 5-inch Dumont phototube mounted inside a large aluminum can with a removable light-tight cover. Here a sample container is seen that can be either a quartz cell or an ordinary pyrex beaker. The size of the apparatus has been arranged so that sample containers with a range of volumes from about 1 ml. up to 1 liter can be utilized. The purpose of larger volumes of course is to contain the greater quantities of radioactive sample that may be required if the specific activity is low. The container is coupled optically to the lucite light pipe with a little silicone oil. The reflecting dome shown here is used only with the smallest containers. For larger volumes the container itself (with a reflecting plate on top) is painted with a white titanium dioxide-reflecting paint so that the light flashes produced in

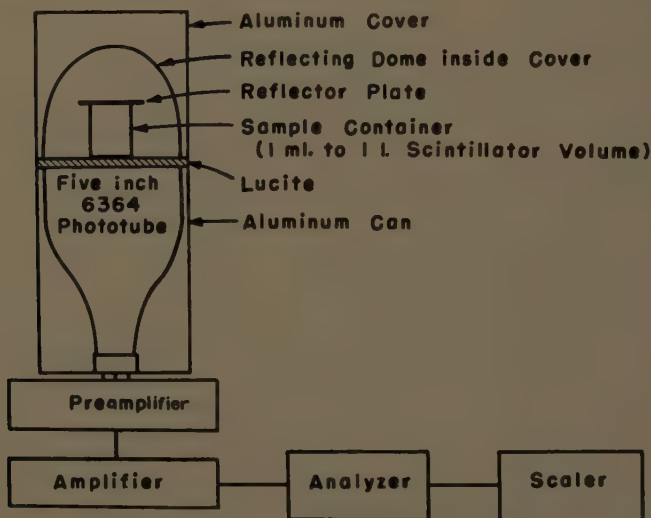


FIGURE 1. Five-inch liquid scintillation counter.

the liquid scintillator are well collected for maximum efficiency into the cathode of the phototube.

The pulses from the phototube are fed through the normal electronics: pre-amplifier, amplifier, analyzer (which may be single-channel or multichannel), and a scaler.

A commercial apparatus that we are also using is shown in FIGURE 2. This is the Tri-Carb counter with which I am sure many of you are familiar. The 2-inch phototubes are contained in a refrigerated chest operated at  $-10^{\circ}\text{C}.$  to minimize phototube noise. This apparatus also employs a coincidence circuit to reduce further the background due to phototube noise. A true event is registered when both phototubes (A and B) "see" the same light flash in the scintillator, whereas the random noise pulses in the two tubes seldom occur simultaneously. Actually, the apparatus is not always used in the coincidence arrangement. In the case of the  $\text{Rb}^{87}$  work, for example, we counted entirely on side A with the lucite light pipe completely covered with reflecting paint

on side B. This mode of operation is then essentially the same as with the 5-inch counter. The reason for this is that we want to maximize collection of the light available from the scintillation into one phototube; otherwise, there is danger of losing some of the beta counts in the very low energy region. However for higher energy betas (for example,  $K^{40}$ ) the coincidence mode may be used and in fact the same answer is obtained both ways, in coincidence and

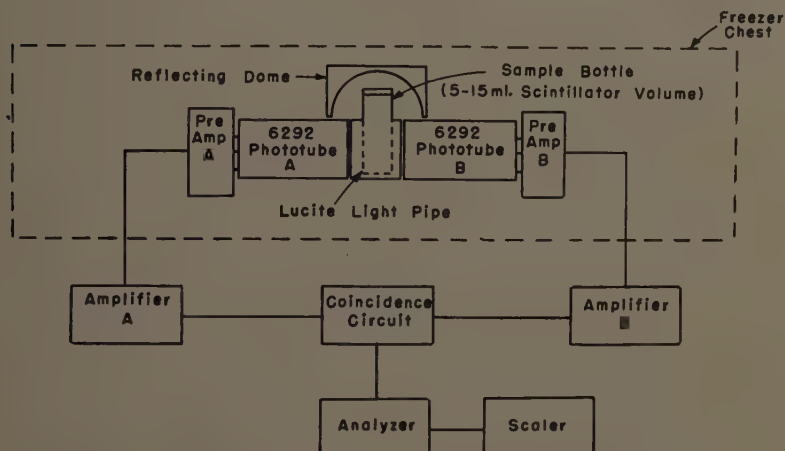


FIGURE 2. Tri-Carb liquid scintillation counter.

TABLE 1  
LIQUID SCINTILLATION-COUNTING EFFICIENCY

Isotope	$\beta^-$ Energy (Mev)	Absolute count d./m.	Liquid scintillation counting	
			d./m.	efficiency (%)
$P^{32}$	1.7	47,400	47,200	$99.6 \pm 1$
$Pm^{147}$	0.22	125,500	126,000	$100.4 \pm 1$
$S^{35}$	0.167	64,880	65,000	$100.2 \pm 2$
$Ru^{106}$	0.040	9,900	8,500	$85.9 \pm 5$
$H^3$	0.018	149,200	120,000	$80.4 \pm 2$

\* Disintegrations, d.

without. The coincidence feature of the Tri-Carb may also be used to advantage in alpha counting.

Let us now consider some evidence on the behavior of the liquid scintillator as an absolute (100 per cent efficiency) counter. TABLE 1 presents data on counting efficiency of the liquid scintillation method as a function of beta energy for various beta emitters (Column 1) with maximum beta energies (Column 2) ranging from 1.7 Mev ( $P^{32}$ ) down to 18 Kev ( $H^3$ ). In Column 3 are shown the absolute counting rates obtained by standard methods. For  $P^{32}$ ,  $Pm^{147}$ , and  $S^{35}$ , absolute counting was done in a conventional  $4\pi$  counter. In this method is counted an essentially weightless source of the beta activity deposited on an essentially weightless film under conditions of 100 per cent ( $4\pi$ )



geometry, that is, with the detector completely surrounding the sample. This absolute counting method is known to be good, except for very low-energy beta emitters, to the order of 1 per cent by intercomparison among several laboratories. As shown by the data in Columns 4 and 5 the liquid scintillation-counting rates are in excellent agreement with the  $4\pi$  counting, indicating an efficiency of 100 per cent for these higher energy betas.

In the case of  $\text{Ru}^{106}$  we are operating in the very low energy region at 40 Kev, and conventional  $4\pi$  counting becomes very difficult because absorption of the low energy betas in either the sample or the film may result in an appreciable loss in counting rate. We therefore resorted to a little "trick." The 1-year  $\text{Ru}^{106}$  decays to a short-lived daughter, 30-sec.  $\text{Rh}^{106}$ , which is a high-energy (about 3 Mev) beta emitter; the soft beta radiation of  $\text{Ru}^{106}$  and the hard beta radiation of  $\text{Rh}^{106}$  are thus in radioactive equilibrium and their disintegration rates are equal. Integral-counting rate curves were obtained for the equilibrium mixture of  $\text{Ru}^{106}$ - $\text{Rh}^{106}$  in the liquid scintillator and resolved into the two beta components. Since the counting efficiency for the hard betas of  $\text{Rh}^{106}$  must be 100 per cent (as previously shown for the beta emitters in the higher energy region), the relative counting rate of the soft beta component due to  $\text{Ru}^{106}$  gives directly the efficiency value of about 86 per cent shown in Column 5.

For the determination of the counting efficiency of tritium ( $\text{H}^3$ ) a standard source of tritiated toluene was used, the absolute disintegration rate (Column 3) of which is known within an error of 2 or 3 per cent by intercomparison checks among several laboratories. The liquid scintillation-counting efficiency for the 18 Kev  $\beta$ -radiation of  $\text{H}^3$  was found to be about 80 per cent as shown in Column 5.

The data in TABLE 1 were obtained with the Tri-Carb counter in the single-phototube mode of operation. With the exception of slightly higher counting efficiencies for  $\text{Ru}^{106}$  and  $\text{H}^3$ , similar results were observed with the 5-inch counter. From these data it is evident that the liquid scintillation-counting method has an efficiency of 100 per cent for  $\beta$ -spectra of maximum energy above approximately 150 Kev. At lower beta energies, however, the counting efficiency decreases because a significant number of  $\beta$ -particles in the spectrum are emitted with insufficient energy to produce a detectable quantity of light in the scintillator. We, as well as other investigators at the Argonne Laboratory, are now engaged in a study of the problem of liquid scintillation counting efficiency for very low energy  $\beta$ -spectra.

To summarize: We have found that the liquid scintillator behaves as an absolute  $\beta$ -counter for spectra of maximum energies above approximately 150 Kev with an over-all reliability of 1 to 2 per cent. I might mention also that the liquid scintillator is an excellent absolute  $\alpha$ -counter as shown by comparison with conventional  $\alpha$ -counters in our laboratory.

As regards the liquid scintillation-counting and half-life determination for  $\text{Rb}^{87}$ , FIGURE 3 shows typical integral counting rate curves obtained with both counters for  $\text{Rb}^{87}$ . Similar data for the somewhat softer  $\beta$ -spectrum of  $\text{S}^{35}$  are plotted in the upper part of the figure for comparison. The background counts include phototube noise and, in fact, consist dominantly of this effect in the lower pulse-height region. Note that the curves extrapolate to the same total

disintegration rates for the two counters and that the required extrapolation of counting rate is small, particularly with the Tri-Carb counter where photo-tube noise was lower. As shown previously in TABLE 1 the extrapolated liquid scintillation-counting rate for  $S^{35}$  is in agreement with standard  $4\pi$  counting.

Data for the determination of the half life of  $Rb^{87}$  are presented in TABLE 2. The nature and source of the rubidium samples used are listed in the first column. Source I was used without purification, although it was found to con-

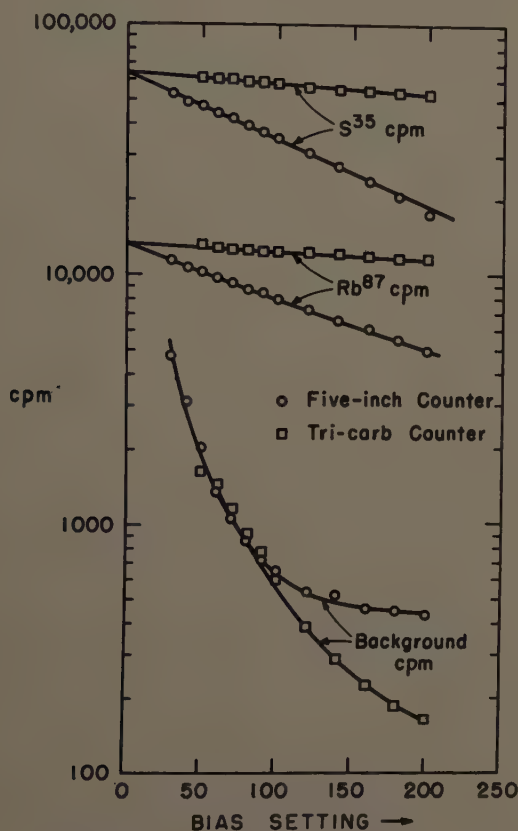


FIGURE 3. Integral-counting rate curves.

tain about 1.5 per cent of alkali metal impurity, chiefly potassium. Since potassium is much lower in specific activity than rubidium, there is no significant error in counting rate, but a correction is required in the gravimetric assay for rubidium as shown in Column 3. Source II is the same material purified by ion exchange. Here a large source (about 1 gm. of rubidium salt) is put through a Dowex-50 ion-exchange column, eluting with dilute hydrochloric acid. This procedure tends to free the rubidium from other alkali metals and also from many elements in the rest of the periodic table. The remaining samples are other sources purified in the same way by ion exchange.

In the second column are the measured counting rates from separate runs using both instruments at random. Results of gravimetric assays for rubidium (by ignition to the sulfate) are given in Column 3. As is apparent, the precision of the data is excellent. Values for the specific activity of rubidium and the corresponding half life of  $\text{Rb}^{87}$  were calculated from these data for the five sources and are shown in Columns 4 and 5. The average value for the half life is  $47.0 \times 10^9$  years with a mean deviation of 1 per cent. Our estimate

TABLE 2  
DATA FOR DETERMINATION OF HALF LIFE OF RUBIDIUM 87

Rubidium source	Activity (d./m./ml.)	Weight of Rb (mg. $\text{Rb}_2\text{SO}_4$ /ml.)	Specific activity of Rb (d./m./mg.)	Half life ( $10^9$ yr.)
I $\text{RbCl}$ (DeRewal, 98.5%)* Average	12400 12500 12500 $12470 \pm 43$	$365.2 \times 0.985 = 359.7$	54.13	47.75
II $\text{RbCl}$ (DeRewal, purified by ion exchange)* Average	11800 12000 12200 12000 12300 $12060 \pm 152$	342.5 341.9 343.6	54.97	47.03
III $\text{RbNO}_3$ (Mackay, purified by ion exchange)† Average	$12300 \pm 100$	348.6 345.5 348.8 $347.6 \pm 1.4$	55.28	46.77
IV $\text{RbCl}$ (Fairmount, purified by ion exchange)‡ Average	13600 13650 13500 $13580 \pm 57$	378.0 377.5	56.14	46.04
V $\text{RbCl}$ (Fairmount, purified by ion exchange)‡ Average	12450 12700 $12580 \pm 125$	361.7 361.3 $361.5 \pm 0.2$	54.36 55.0 $\pm 0.6$	47.56 $47.0 \pm 0.5$

\* DeRewal International Rare Metals Co., Philadelphia, Pa.

† A. D. Mackay, Inc., New York, N.Y.

‡ Fairmount Chemical Co., New York, N.Y.

of the over-all uncertainty in this determination is 2 per cent based primarily on a consideration of the absolute counting method. We feel that this is a definitive measurement of the half life of  $\text{Rb}^{87}$ .

Before proceeding with a discussion of similar measurements on  $\text{K}^{40}$ , it might be useful to consider briefly the decay scheme.<sup>4</sup> In comparison with the simple  $\beta^-$  decay of  $\text{Rb}^{87}$ , the radioactive decay of  $\text{K}^{40}$  is more complex and additional problems are encountered. About 90 per cent of the decay of  $\text{K}^{40}$  occurs by 1.33 Mev  $\beta^-$  emission directly to the ground state of  $\text{Ca}^{40}$  and about 10 per cent by electron capture to an excited state of  $\text{Ar}^{40}$  that undergoes a 1.46 Mev  $\gamma$



transition to the ground state. The partial decay constant for the  $\beta^-$  branch is determined of course from the specific  $\beta^-$  activity of potassium, and this aspect of the problem has been attacked successfully by the same method as just described for rubidium. The partial decay constant for the electron capture branch is determined from the specific  $\gamma$  activity on the assumption that essentially all of this mode of decay goes through the excited level in  $\text{Ar}^{40}$ . Appreciable electron capture directly to the ground state of  $\text{Ar}^{40}$  remains a possibility, however, and we are now engaged in experiments designed to settle this question and thus to make more reliable the partial decay constant for electron capture based on specific  $\gamma$  activity.

According to theory, a good discussion of which has been given by Morrison,<sup>5</sup> positron ( $\beta^+$ ) emission by  $\text{K}^{40}$  to the ground state of  $\text{Ar}^{40}$  should occur with a frequency of about  $10^{-5}$  with respect to  $\beta^-$  decay (or about  $10^{-4}$  with respect to  $\gamma$  emission), and the ratio of electron capture (ground state) to  $\beta^+$  emission must be close to 100. If a limit on  $\beta^+$  decay could be established at this level, we could then be confident that electron capture to the ground state represents only about 1 per cent of the total decay of  $\text{K}^{40}$  to  $\text{Ar}^{40}$ .

The apparatus for this investigation consists of three scintillation detectors in a triple coincidence arrangement. Two of the detectors are NaI crystals situated co-linearly on each side of the  $\text{K}^{40}$  source and electronically gated to accept the two 0.51 Mev annihilation  $\gamma$  rays resulting from  $\beta^+$  decay. The third detector is a liquid scintillator solution (about 5 ml. in volume) containing a highly enriched source of  $\text{K}^{40}$  (about 40 mg. of potassium enriched in  $\text{K}^{40}$  to the equivalent of 100 gm. of natural potassium). The pulse-height spectrum of the positrons in the liquid scintillator in coincidence with the annihilation quanta is fed to a 256-channel analyzer. With this arrangement the background is very low, and we hope to be able not only to set a good upper limit on positron emission but actually to determine the frequency of this mode of decay. Careful measurements of the specific  $\gamma$  activity of the enriched source will also be made to complete the investigation of the decay constants for  $\text{K}^{40}$ .

It should be mentioned at this point that, shortly after we undertook the search for positron emission by  $\text{K}^{40}$ , Tilley and Madansky<sup>6</sup> reported the results of a similar experiment. Their method is the same as ours with the exception that they employed a KI scintillation crystal (containing about 50 gm. of natural potassium) as the third detector and source of  $\text{K}^{40}$ . Two drawbacks were encountered with this source: namely, interference by a large pair production peak at 0.44 Mev caused by interaction of the 1.46 Mev  $\gamma$  rays of  $\text{K}^{40}$  with the massive KI crystal and an uncertain background estimated from a substitute NaI crystal. In spite of these disadvantages they were able to set an upper limit of about  $2 \times 10^{-5}$  for the ratio of  $\beta^+$  to  $\beta^-$  emission in the decay of  $\text{K}^{40}$ . This is the first useful result to be published on this point and it indicates, as I have just mentioned, that no more than about 2 per cent of the electron capture decay goes directly to the ground state. We shall proceed with our experiment, however, because of the advantages of low pair production effect and greater certainty in background offered by the liquid scintillator source.

Experimental data for the determination of the partial half life for  $\beta^-$  decay of  $\text{K}^{40}$  are presented in FIGURE 4 and TABLE 3. Note that the required extrapolation of the integral-counting rate curve for  $\text{K}^{40}$  is very small (about 1 per cent)

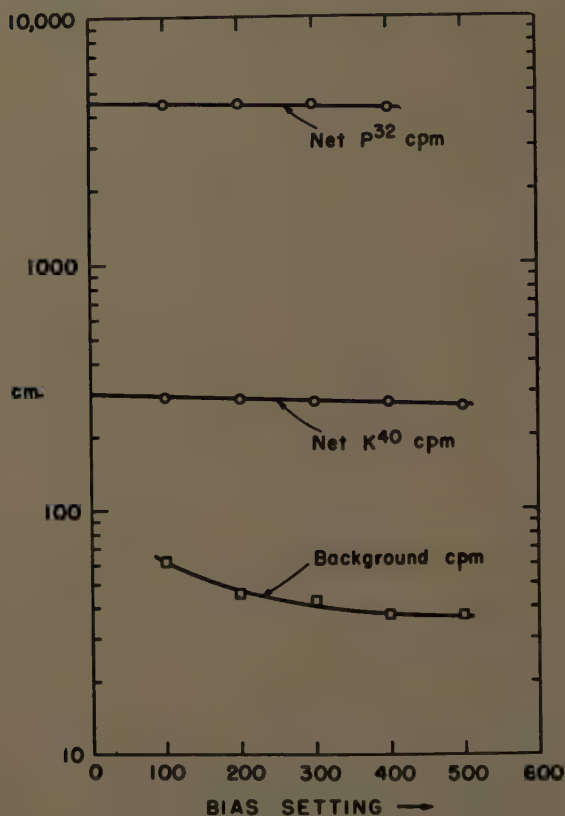


FIGURE 4. Integral-counting rate curves.

TABLE 3  
DATA FOR DETERMINATION OF HALF LIFE OF POTASSIUM 40

Potassium source	Activity $\beta^-/\text{sec.}$	Weight of K (mg.)	Specific activity of K $\beta^-/\text{sec./gm.}$	$\beta^-$ Half life ( $10^9$ yr.)
I KOH (Merck, reagent grade)	7.12	250.7	28.4	1.40 <sub>5</sub>
II KOH (purified by ion ex- change)	5.18	185.6	27.9	1.43 <sub>0</sub>
III KOH (purified by ion ex- change)	3.43	120.4	28.5	1.40 <sub>0</sub>
	3.22	115.8	27.8	1.43 <sub>5</sub>
	3.18	114.5	27.8	1.43 <sub>5</sub>
	3.23	113.2	28.5	1.40 <sub>0</sub>
	4.85	169.9	28.5	1.40 <sub>0</sub>
	4.60	161.8	28.4	1.40 <sub>5</sub>
Average			$28.2 \pm 0.3$	$1.41_5 \pm 0.015$

owing to the higher energy of the  $\beta$ -spectrum. Similar data for  $P^{32}$  and the background of the counter are shown for comparison.

The potassium source in all cases was Merck (reagent grade) potassium hydroxide. Optical spectrographic analysis showed the only significant impurity to be 0.1 per cent sodium, and radioactivation analysis demonstrated the absence of rubidium and cesium. However, just to be sure, Samples II and III were put through the ion-exchange column and the same specific activity was obtained, indicating that the purity of the source material is satisfactory.

The gravimetric method is the same as was used for rubidium. Each value of the specific  $\beta^-$  activity of potassium given in TABLE 3 is the result of a separate count and gravimetric assay of the counted sample and includes a small correction (0.5 per cent) for the response of the liquid scintillator to the  $\gamma$  rays of  $K^{40}$ .

The observed specific  $\beta^-$  activity of natural potassium is  $28.2 \pm 0.3$  d./sec./gm. With a value<sup>4</sup> of 0.0118 per cent for the isotopic abundance of  $K^{40}$ , this corresponds to a  $\beta^-$  half life of  $(1.42 \pm 0.02) \times 10^9$  years. Using the currently accepted value<sup>1,4</sup> of  $0.11 \pm 0.02$  for the electron capture branch, the total half life of  $K^{40}$  is  $(1.26 \pm .04) \times 10^9$  years.

To conclude this discussion I mention the work we are now undertaking on the decay constants of  $U^{235}$ ,  $U^{238}$ , and  $Th^{232}$ . Our interest in this endeavor stems largely from the stimulating contacts I had with J. L. Kulp last year in England. He pointed out that ages determined by the U-Pb and Th-Pb methods are often in disagreement and that there is sufficient interest in these decay constants among geochronologists to merit the effort involved in making accurate redeterminations in spite of the apparent precision of the constants indicated in the literature.

In an excellent paper<sup>2</sup> published in 1952, Fleming *et al.* reported a half life for  $U^{235}$  with an error of about 2 per cent. They used an enriched source of  $U^{235}$  containing 0.022 per cent  $U^{234}$  that contributed 35 per cent to the total  $\alpha$  activity. Their estimated error is almost entirely due to interference by the  $\alpha$  rays of  $U^{234}$  that tend to overlap the  $U^{235}$   $\alpha$ -peaks in the pulse analysis. In our work we shall use an enriched  $U^{235}$  source in which the interfering  $\alpha$ -activity of  $U^{234}$  is only about 3 per cent, therefore causing very little error in pulse analysis. Thus essentially we intend to repeat their work on  $U^{235}$  with a superior source, doing it in much the same way. Absolute counting will be done with a calibrated intermediate-geometry  $\alpha$ -counter that, incidentally, is in excellent agreement with absolute counting by the liquid scintillation method. Gravimetric and perhaps also volumetric methods will be used for uranium assay.

The half life of  $U^{238}$  will be determined in a similar manner using highly depleted uranium in which the  $\alpha$ -activity due to  $U^{235}$  and  $U^{234}$  is essentially negligible. Although there is excellent agreement among the several values for the half life of  $U^{238}$  reported in the literature,<sup>1</sup> the determination of specific activity on an isotopically pure source in a direct method such as we are using has been made by only one investigator.<sup>7</sup>

Finally, in the case of  $Th^{232}$  for which there appears to be the most uncertainty in the decay constant,<sup>1</sup> determination will be made of the specific activity of purified thorium by absolute  $\alpha$ -counting in a liquid scintillator combined with assay of thorium by an accurate titrimetric method. The thorium used in this

work is to be freshly separated from monazite sand to ensure radioactive equilibrium (equal activities) for  $\text{Th}^{228}$  and  $\text{Th}^{232}$  and a small correction for the presence of  $\text{Th}^{230}$  (decay product of uranium) to be determined by  $\alpha$ -pulse analysis. The method is simple and direct and should provide a decay constant with high accuracy.

In conclusion, I reiterate that the currently accepted decay constants for uranium and thorium are probably accurate to the order of 2 per cent; although we may not be able to improve on this, we shall attempt it in any case.

### Summary

The decay constants of interest in the geochronology of rock systems are those of  $\text{Rb}^{87}$ ,  $\text{K}^{40}$ ,  $\text{U}^{235}$ ,  $\text{U}^{238}$ , and  $\text{Th}^{232}$ . The U-Pb and Th-Pb methods have long been used in measurements of geological ages and, in recent years, the increasing usefulness and significance of the Rb-Sr and K-Ar methods have been demonstrated. A survey of the literature clearly indicates the need for more accurate determinations of the decay constants of  $\text{Rb}^{87}$ ,  $\text{K}^{40}$  and, possibly,  $\text{U}^{235}$ . The recently developed technique of absolute counting in a liquid scintillator has been applied successfully to definitive measurements of the constants for  $\beta^-$  decay of  $\text{Rb}^{87}$  and  $\text{K}^{40}$ . In this method the alkali element source in the form of an organic salt is dissolved in the liquid scintillating detector and counted in "4 $\pi$  geometry" without the usual problem of self-absorption encountered with thick sources. The observed  $\beta^-$ -decay constant of  $\text{Rb}^{87}$  is  $(1.47 \pm 0.03) \times 10^{-11} \text{ yr.}^{-1}$  corresponding to a half life of  $(4.70 \pm 0.10) \times 10^{10} \text{ yr.}$  The partial decay constant for  $\beta^-$  decay of  $\text{K}^{40}$  to  $\text{Ca}^{40}$  is found to be  $(4.90 \pm 0.07) \times 10^{-10} \text{ yr.}^{-1}$  corresponding to a partial half life of  $(1.42 \pm 0.02) \times 10^9 \text{ yr.}$  Work is in progress to obtain an accurate value of the partial decay constant for electron capture to  $\text{Ar}^{40}$  by NaI scintillation counting of the 1.46 Mev  $\gamma$  rays emitted in this decay branch. An attempt is also being made to diminish the present uncertainty of a few per cent in the decay constant of  $\text{U}^{235}$  by absolute  $\alpha$ -counting and pulse analysis of a highly enriched source containing an order of magnitude less of the interfering  $\alpha$ -activity of  $\text{U}^{234}$  than was previously available. The decay constant of  $\text{U}^{238}$  will be determined similarly using uranium highly depleted with respect to  $\text{U}^{235}$  and  $\text{U}^{234}$ . A method based on absolute  $\alpha$ -counting in a liquid scintillator will be employed in the case of  $\text{Th}^{232}$ .

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### Discussion of the Paper

G. W. WETHERILL (*Carnegie Institution of Washington, Washington, D.C.*): In the  $\text{Rb}^{87}$  determination, how much extrapolation was there from what you actually found, down to the extrapolated counting rate or, to say it another



way, what is the limit on the half life that could be established this way with the counting rate?

GLENDENIN: For  $K^{40}$  this is very small, but in the case of  $Rb^{87}$  we do have a source of error in the extrapolation of the integral counting curves. The required extrapolation was 5 per cent for the Tri-Carb counter and therefore the half life of  $Rb^{87}$  cannot be longer than  $49.5 \times 10^9$  years even if no extrapolation were made. We feel, however, that the error from this source is probably not greater than 2 per cent.

WETHERILL: What about the difference in the  $\beta$ -energy spectrum of  $Rb^{87}$  compared to  $S^{35}$  in the low energy region?

GLENDENIN: The  $\beta$ -decay of  $Rb^{87}$  is highly forbidden, and the spectrum has a much lower average energy than allowed spectra of about the same maximum energy (such as  $Ca^{45}$ ). The  $\beta$ -spectrum of  $Rb^{87}$  has an excess of electrons in the low energy region. We did notice however, and this is the reason for showing  $S^{35}$  in comparison, that as far as the initial slope of the integral counting curve is concerned, which is a reflection of the average energy of the  $\beta$ -spectrum,  $S^{35}$  and  $Rb^{87}$  are comparable. They have about the same slope.

WETHERILL: However it began to appear as if the last point on the rubidium curve were above the line rather than on the line.

GLENDENIN: It is in this particular curve, but many of them have been run and there is no significant trend.

WETHERILL: Also, may I ask about this enriched  $K^{40}$  that you are going to use for the electron capture data. What is the isotopic abundance of the  $K^{40}$ ?

GLENDENIN: I think it is approximately 30 per cent.

WETHERILL: Previous workers using enriched sources have failed to measure the isotopic abundance of the  $K^{40}$ . This really deserves careful attention. May I ask also about this electron capture to  $\beta^+$  ratio of 100. As far as anything I have seen in the literature is concerned, the only estimate of this transition is that of Fireman years ago. He calculated a figure of 600.

GLENDENIN: In a theoretical analysis of the  $K^{40}$  decay scheme Morrison (1951) agreed with Fireman (1949) that this ratio is independent of nuclear matrix elements and dependent only on the energy available for  $\beta^+$  decay. He stated that his recalculations differ slightly from the results of Fireman and that for a  $\beta^+$  energy of 0.5 Mev ( $K^{40}/Ar^{40}$  mass difference) the ratio is close to 100. Brosi and Ketelle of the Oak Ridge National Laboratory, Oak Ridge, Tenn. have recently recalculated this ratio and have a value of 130.

Admittedly the measurement of  $\beta^+$  decay by  $K^{40}$  is an indirect handle on the situation and it is too bad that the electron captures cannot be counted directly with sufficient accuracy, but it is a very difficult thing to do with such low energy X rays or Auger electrons.

QUESTION: Regarding the extrapolation of the counting rate, does theory make any definite statement about the validity of that extrapolation?

GLENDENIN: I did not want to go into this because it actually goes back to the intrinsic response of the liquid scintillator solution.

The liquid scintillator that we use has a response such that approximately two kv. of electron energy must be expended in the liquid scintillator on the average to make one effective photo-electron at the photocathode, that is, to make a detectable pulse.

Therefore for  $\beta$ -particles in the spectrum near or below this energy it is to be expected from statistical distribution that there will be some detection failures and, indeed, in the counting of  $H^3$  or  $Ru^{106}$  as we have seen, the extrapolated counting rate falls short of 100 per cent. The detector may be considered to have a low energy cut-off. Horrocks and Studier (article in preparation) have shown that this effect can be calculated quantitatively from the Fermi function for a given  $\beta$ -spectrum, probability statistics, and the intrinsic response of the scintillator. The counting efficiencies of the liquid scintillator for  $H^3$  and  $Ru^{106}$  calculated in this way agree very well with the observed values.

Fortunately, in rubidium and potassium, the  $\beta$ -spectra are of sufficient energy that very little loss in counting efficiency is expected, and the data for  $S^{35}$  seen in TABLE 1 lend support to this view.

QUESTION: Did I understnad that you did not use enriched samples in your  $Rb^{87}$  and  $K^{40}$  work?

GLENDENIN: No.

QUESTION: Why not?

GLENDENIN: We thought it better to use the natural element for which someone, such as A. O. C. Nier, has determined the isotopic composition accurately rather than to get the enriched element and then be faced with the additional problem (and error) of measuring abundance. I prefer to rely on the natural elements.

QUESTION: Did you have isotopic analyses done on your samples?

GLENDENIN: You mean the natural elements used?

QUESTION: Yes.

GLENDENIN: No, we used the literature values of 27.85 per cent and 0.0118 per cent for  $Rb^{87}$  and  $K^{40}$ , respectively.

QUESTION: A point I think is bothering a lot of us that I would like to pursue here is the shape of the  $\beta$ -spectrum curve. Suppose it went up sharply in the low energy region below the first observed point?

GLENDENIN: I really cannot answer that question except to say that it is unlikely that a  $\beta$ -spectrum would rise abruptly in the energy region of the first few kv.

A. O. C. NIER (*University of Minnesota, Minneapolis, Minn.*): I was pleased to hear that fine compliment. I might say that that work was done about 10 or more years ago. When separated, isotopes were still supposed to be secret, and those of us outside the fences did not have access to it, but we did the best we could without it.

Now that you can get separated isotopes in these things and measure these decay constants so accurately, it would be well worthwhile for someone else to examine potassium, rubidium, and other elements, because some of those measurements, as is known, are indirectly calibrated with others such as argon. These calibrations, I think, are pretty good but, with improvements being made everywhere and better equipment available, it is really too bad to overlook this part. Therefore I urge those who have the facilities to work on this problem.

GLENDENIN: Yes, it would seem worthwhile, particularly in the case of  $K^{40}$ ; we may look into this.

WETHERILL: I think it should be pointed out that, in addition to the ability of Nier to measure isotopic abundance, there is another advantage in using

natural material. That is, as this decay constant is eventually used in the age equations for the compilation of ages measured on natural potassium and natural rubidium, the isotopic abundance, the natural isotopic abundance, of  $K^{40}$  and  $Rb^{87}$  cancel out in the equation if the decay constant is measured on material of the same isotopic abundance. If it is on different material, there is always an error due to both the natural abundance and the material used.

W. H. PINSON (*Massachusetts Institute of Technology, Cambridge, Mass.*): May I ask just one or two general questions about the chemistry used. How was the purity of the rubidium samples verified after they had been run through the ion-exchange column? Were they weighed as rubidium sulfate?

GLENDENIN: We had optical spectroscopic analyses made on the sources both before and after purification, and we also did radioactivation analysis. The only significant impurities found are other alkali elements. In the case of potassium, for example, rubidium and cesium were both in the range of 30 parts per million while sodium was about one tenth of 1 per cent.

PINSON: How much potassium was in the rubidium?

GLENDENIN: In the case of rubidium the potassium in a typical untreated sample was about  $1\frac{1}{2}$  per cent. After purification with the ion-exchange column, the potassium impurity was down to a few tenths of one per cent.

PINSON: The experience that I have had in working with the Fairmount rubidium (one of the sources you used) is that initially we have about 10 to 12 per cent of potassium impurity and, after purification through the ion-exchange columns a few times, there is still a measurable amount (approximately 1 per cent potassium) left in the samples. Also, we thought there was an observable change in isotopic composition of the rubidium after it had been run through the columns a few times, the 85/87 ratio changing from 2.59 to 2.52; this was carefully examined.

GLENDENIN: I suggest that this is doubtful because it is so difficult just to separate potassium from rubidium, at least on the macroscopic level. A separation of isotopes, therefore, seems unlikely.

QUESTION: There seems to be a great deal of concentration on the cationic impurities in these salts. There are anions in these salts and it is obligatory for an investigator to demonstrate in any one of these gravimetric things, although it is easier to send it to an optical spectrographer, that what is being weighed is a stoichiometric formula. It is in fact most desirable to return to gravimetric (or what would constitute atomic weight) determinations and to verify by good analytical procedure that it is  $RbCl$ ,  $KCl$ , or  $KOH$ , in which there can be a large number of other anion impurities that are just as serious as the cationic impurities.

GLENDENIN: In our work we do not rely on  $KCl$  or whatever the compound may be initially. The elements in the form of an organic compound in the liquid scintillator are wet-ashed with nitric, perchloric and, finally, sulfuric acid, and ignited to the sulfate by a classical gravimetric method. From my knowledge of quantitative analysis this method should be good to a few tenths of 1 per cent.

PINSON: Is there no possibility of getting potassium acid sulfate in there too?

GLENDENIN: Yes, there is. In standard reference books on quantitative analysis it is pointed out that caution must be exercised with potassium, ru-

bidium, or cesium so that the acid sulfate is not obtained, and, of course, the analysis must be done correctly. The sample must be treated with ammonium carbonate, ignited, and the process repeated until constant weight is achieved to make certain that the acid sulfate has been eliminated.

QUESTION: I think, in addition, that it is possible to do very simple chemical conversions to other salts and to verify that in different molecular compounds the same weight of potassium is found.

GLENDENIN: As a matter of fact, we have done this on occasion. For example, we have weighed potassium as the chloride, converted to the sulfate, and reweighed. We find the same weight of potassium with both salts.

QUESTION: Could you differentiate that integral counting curve for rubidium at the first point?

GLENDENIN: If you mean at what energy does this point occur in the spectrum or where does photonoise become serious on an electron energy scale, it is the last significant count that can be taken before the photonoise becomes prohibitive. This point lies at about 5 to 10 Kev. We must of course extrapolate back to zero through this photonoise region.

L. T. ALDRICH (*Carnegie Institution of Washington, Washington, D.C.*): Huster, Institut für Kernphysik der Universität Munster, German Federal Republic, just wrote that he has gone down to  $10 \mu\text{g./cm.}^2$  with  $4\pi$  counting of rubidium. He feels that he cannot go higher (longer) than  $4.7 \times 10^{10}$  years for the half life of  $\text{Rb}^{87}$ .

GLENDENIN: Can he go lower? We have a feeling that, if there is any error, it would be in the direction of a lower (shorter) half life.

ALDRICH: Not unless more rubidium is present than thought. If you start with your scintillator and wet-ash to the sulfate, this involves perchloric acid, does it not?

GLENDENIN: It is a sulfuric, perchloric, nitric, wet-ashing that concludes the analysis, with just sulfuric acid taken to produce dryness in the platinum dish and finally to ignite to the sulfate.

ALDRICH: The problem then is to eliminate all the perchloric. This is the only question I have because this might make an error the other way. Everything else would make the half life lower. This is the only thing that I have any question about, and I do not know whether the chemists agree.

QUESTION: I do feel that in the discussion of these results the chemical aspect of it should be treated with absolute thoroughness because there is a great deal of room for possible error in the weighing of rubidium salts, the purification, and the isotope composition.

GLENDENIN: I suppose that as a chemist I am guilty of not worrying too much about the chemistry, but am taking it for granted. I worry more about the physical aspect of the problem, that is, the determination of activity, than the chemical assay of rubidium or potassium, which I believe to be quite accurate.

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## THE RUBIDIUM-STRONTIUM METHOD

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One of the problems that is particularly important in measuring ages using the Rb-Sr and the U-Th lead systems is the isotopic composition of any original daughter element occurring in the mineral under investigation. As long as it is possible to get minerals having a high ratio of parent or radioactive material to daughter element, this is not a problem. In the early work on the Rb-Sr method, lepidolites and muscovites were available that had 2 or 3 per cent rubidium or at least several thousand ppm. No one was concerned much about what might be the isotopic composition of the original strontium that occurred in the muscovite or lepidolite because there was no original strontium in some of these minerals.

However, as this method has been pushed closer to the limit and work has been done with minerals having substantial amounts of original strontium in them, the question of what the isotopic composition of this strontium might be like or, specifically, what the isotopic abundance of the strontium-87 in the original strontium was becomes more and more important. There will be, I am sure, several later discussions that involve an answer to this question.

I have been interested in the problem not only from this point of view but from a more general point of view, namely, the distribution of the radiogenic strontium in the earth's crust. Just what happens to the radiogenic strontium formed from rubidium? How does it get distributed between various geochemical reservoirs? Where does it end up? Does it accumulate in certain types of rock?

We have determined the isotopic composition of strontium from a variety of igneous, metamorphic, and sedimentary rocks. The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios of a number of volcanic rocks are shown in TABLE 1.

The major uncertainty in these isotope ratios arises from an isotope fractionation effect that has been observed in some runs. We have rather arbitrarily assumed that the  $\text{Sr}^{86}/\text{Sr}^{88}$  ratio of all of these rocks is constant to approximately 0.2 per cent. Some of the runs made here showed no fractionation. We have adopted the 86/88 ratio of these runs as the correct ratio and corrected the runs showing fractionation from this ratio. Thus all 87/86 ratios were corrected to an  $\text{Sr}^{86}/\text{Sr}^{88}$  ratio of 0.1186. It has been observed that where duplicate runs were made the agreement of the corrected  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios has been better than the raw ratios.

The basalt ratios seen here are almost within experimental agreement ranging from 0.704 to 0.712.

Similar measurements have been made on strontium extracted from sea water, shells growing in sea water, and from limestones of different ages. These are shown in TABLE 2. The ratios for sea water are very constant, ranging from 0.711 to 0.712.

Three limestones have been measured ranging from an Ordovician limestone to a very old Pre-Cambrian limestone in an attempt to see how this ratio might vary with geologic time; essentially no variation was found. The old

Pre-Cambrian limestone, which is from a terrain older than 2.6 billion years (b.y.), gives a ratio of 0.705. The difference between this and modern ocean water is significant but not extraordinary. It is certainly not a useful way of dating limestones. The picture is one of a constant ratio. The most interest-

TABLE 1  
ISOTOPIC COMPOSITION OF STRONTIUM FROM VOLCANIC ROCKS

Sample	Sr <sup>86</sup> /Sr <sup>88</sup>	Sr <sup>87</sup> /Sr <sup>88</sup>	Sr <sup>87</sup> /Sr <sup>86</sup>
Olivine, basalt Kilauea, Hawaii	0.1183	0.0837	0.708
Leucitite Lake Kivu, Africa	0.1186	0.0840	0.708
Triassic diabase (W-1) Centerville, Va.	0.1196 (0.1186)	0.0846 (0.0842)	0.707 (0.710)
Anorthosite Stillwater Complex, Mont.	0.1187	0.0843	0.711
Keewatin pillow lava Lac du Bonnet, Man., Canada	0.1185	0.0844	0.712

TABLE 2  
ISOTOPIC COMPOSITION OF STRONTIUM FROM OCEANIC MATERIALS

Sample	Sr <sup>86</sup> /Sr <sup>88</sup>	Sr <sup>87</sup> /Sr <sup>88</sup>	Sr <sup>87</sup> /Sr <sup>86</sup>
Sea water mid-Atlantic	0.1182 (0.1186)	0.0844 (0.0846)	0.713 (0.712)
Acantharia shell Long Island Sound	0.1173 (0.1186)	0.0840 (0.0845)	0.716 (0.712)
Globigerina ooze Core A-167	0.1185	0.0843	0.711

TABLE 3  
ISOTOPIC COMPOSITION OF STRONTIUM IN GRANITIC ROCKS

Location	(Sr <sup>87</sup> /Sr <sup>86</sup> ) <sub>D</sub>	Rb/Sr	(Sr <sup>87</sup> /Sr <sup>86</sup> ) <sub>0</sub>	Age (m.y.)
Westerly, R.I.	0.719	0.85	0.713 ± .004	170
Llano County, Texas	0.741	0.64	0.710 ± .004	1100
Doyleville, Colo.	0.936	3.62	0.726 ± .017	1400
Virojoki, Finland	0.807	1.43	0.712 ± .008	1630
Espoo, Finland	0.968	3.86	0.726 ± .018	1630
Pernio, Finland	0.858	2.16	0.700 ± .011	1800
Kaavi, Finland	0.740	0.228	0.724 ± .006	1800
Pointe Du Bois, Man., Canada	0.769	0.60	0.708 ± .006	2650
Sheridan, Wyo.	0.750	0.351	0.711 ± .005	2750
Bikita, S. Rhodesia	1.003	2.60	0.733 — .697	2600-2900

ing information as far as age measurements are concerned are the data obtained on a number of different granites (TABLE 3).

This work was done two or three years ago when the selection of dated granites was far from as complete as it would be today. We selected a number of different granites covering most of the time that was then known or most of the age range that was then established.

The ages used in the calculations are given in the last column and perhaps

there is some question about some of them. In some cases, it is a mica age, a Rb-Sr, or K-Ar age; in other cases, particularly samples from Finland, Texas, and Colorado, we have both micas and zircon ages. I think these ages are fairly well established except for the last one, where I think it can only be said that the rock is older than 2600 m.y.

We have also determined the Rb/Sr ratio, that is, the chemical ratio of rubidium to strontium, in these rocks. Using this ratio, the age, and the measured  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio, we calculate the initial 87/86 ratio or the initial abundance of the strontium 87 in these rocks.

As might be expected, there are large variations in the  $\text{Sr}^{87}$  abundance of granites. Some of the strontium in these granites is rather radiogenic yet, when calculated to the initial value, the numbers fall very much in the range found for the basalts and limestones. The large uncertainties in the initial  $\text{Sr}^{87}$  abundances are usually due to errors in the age as well as the uncertainty in Sr/Rb ratio.

The general conclusion is that the initial abundance of strontium-87 in these granitic rocks is no different from that found in the present-day ocean or in the basalts. The basalts cover a rather wide age range, and this is further evidence that the isotopic composition does not change very much over geologic time.

There are a few cases where the numbers are slightly out of line. The Kaavi, Finland sample is somewhat higher than the others, and the Quartz Creek sample is also somewhat higher. In these cases we have used the ages based on biotites. G. R. Tilton has reported (elsewhere on this monograph) a zircon age or zircon Pb-Pb age from the Quartz Creek rock of 1560 m.y., I believe. If that age were to be used, the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio could come down to about 0.710.

The Kaavi sample is perhaps interesting in that it occurs on the boundary of 1800- and 2600-m.y.-old rocks. It is in the kind of situation in which original radiogenic strontium might be expected.

In general it seems that the granitic rocks and the basaltic rocks and the ocean have a similar isotopic composition. When a granite is formed, however, the Rb/Sr ratio may be increased sufficiently for the rock as a whole to be used to determine the age.

In conclusion, in so far as the problem of the original  $\text{Sr}^{87}$  abundance is concerned, I think that this is not much of a problem with a normal granite, where the  $\text{Sr}^{87}$  abundance appears rather constant. There is one other application here that may be mentioned elsewhere: if a rock is remobilized and then recrystallized as another granite, there is a possibility that this approach can be adopted, using whole rock rather than the individual minerals to find out something about the original age of the granite rather than the time of remobilization or palingenesis. We have found no evidence for this kind of thing in the samples measured other than the two points mentioned.

#### *Discussion of the Paper*

W. R. ECKELMANN (*Jersey Production Research Co., Tulsa, Okla.*): How did you arrive at the error for the specific ages that was then attributed to the 87/86 ratio?



GAST (*University of Minnesota, Minneapolis, Minn.*): There is no real objective way to do this. If there were a concordant zircon that agreed with the biotite age, an error was used of perhaps 2, 3, or 5 per cent. If there were biotite age only, a somewhat higher error was used. This is subjective.

C. MILLER (*University of Rhode Island, Kingston, R.I.*): As regards that Westerley granite, are you sure it was the granite you obtained or a basalt found in the Westerley area?

GAST: The granite used is the G-1 standard distributed by the United States Geological Survey.

MILLER: However the calculation seems to indicate that the Westerley is pre-Pennsylvanian and hence this age would be incorrect.

GAST: In this case the effect of such an error is small. That is, any error in the age given here would have a very small effect on the correction made. The age measurement here is taken from the Massachusetts Institute of Technology Progress Report.

MILLER: We were of the opinion that it was at least 250 m.y. or about that.

GAST: That would not affect what we have said; that is why I said earlier that there may be some quarrels with the ages.

P. M. JEFFERY (*University of Western Australia, Nedlands, Australia*): In the first table a deviation of about 1 per cent was shown and it was said to be not really significant. This is quite true in general. It is not significant except in the case of rocks with a high common strontium content. Under these circumstances, a 1 per cent deviation in the  $\text{Sr}^{88}/\text{Sr}^{86}$  value can be quite significant if the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio is calculated rather than measured.

GAST: It certainly is if something about the age of the rock is to be determined, but this has not been done. If this method were to be used to determine ages, the age would depend, of course on the accuracy of this measurement.

JEFFERY: May I point out that it is essential that the 87/86 ratio should be measured independently. Calculations cannot be made from the 88/86 ratio correction to the 87, at least not with 1 per cent correction  $\text{Sr}^{88}/\text{Sr}^{86}$ .

MILLER: As regards TABLE 3, is the age for the Westerly granite an independent age measurement? I do not understand the process that led to this.

GAST: The ages in the last column of TABLE 3 were all independent age measurements. Most of them were made by other workers.

K. K. TUREKIAN (*Yale University, New Haven, Conn.*): Have any measurements been made on rhyolites or porphyries associated with Laramide events? In the Beartooth Mountains, for example, if the porphyry dykes come from remobilization of the basement rocks they might have measurably higher  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in the common strontium.

GAST: The closest thing to that, which was not reported in the tables, is the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in a leucite-rich basalt from the African Rift Valley for which one of the proposed origins was this type of remobilization process. It came within experimental error of the other basalts.

# METAMORPHIC CHRONOLOGY BY THE RUBIDIUM-STRONTIUM METHOD

W. Compston and P. M. Jeffery

*University of Western Australia, Nedlands, Australia*

The K-Ar and Rb-Sr age methods have often been applied to biotite or feldspar minerals extracted from a granite to determine the age of the granite itself. Before an age determined from such a mineral concentrate can be stated with any confidence to be the age of rock crystallization, it is necessary to have some idea of the metamorphic history of the granite, isotopically speaking and also, with the Rb-Sr method, to know its common strontium isotopic composition when crystallized.

It has been found that a very satisfactory method of examining both the history of a granite and its initial common strontium composition as recorded by Rb-Sr measurements is to present the data graphically.

## *The Graphic Method*

Assuming that the age of a mineral or a total rock sample is the time elapsed since the component under consideration became effectively a closed chemical system for Rb and Sr then its age  $T$  is given (see footnote) by:

$$\lambda T = \ln (1 + {}^*\text{Sr}^{87}/\text{Rb}^{87})$$

$$\therefore T \doteq {}^*\text{Sr}^{87}/\lambda \text{Rb}^{87}$$

The  ${}^*\text{Sr}^{87}$  content can be found since:

$${}^*\text{Sr}^{87} = \text{Sr}^{86} \cdot [\text{Sr}(87/86)_{\text{now}} - \text{Sr}(87/86)_{\text{init}}]$$

$$\therefore T \doteq \text{Sr}^{86}/\lambda \text{Rb}^{87} \cdot [\text{Sr}(87/86)_{\text{now}} - \text{Sr}(87/86)_{\text{init}}]$$

This is the equation of a straight line with gradient  $\text{Sr}^{86}/\lambda \text{Rb}^{87}$  and  $\text{Sr}(87/86)_{\text{init}}$  the independent variable. Each sample will thus have its own individual line when plotted on a graph with axes of  $T$  and  $\text{Sr}(87/86)_{\text{init}}$ . The departure from linearity due to the logarithmic approximation in the above formula, although small, may be avoided completely by considering a dependent variable  $\theta$  related to the above equation by the formula:

$$\theta = \text{Sr}^{86}/\text{Rb}^{87} \cdot [\text{Sr}(87/86)_{\text{now}} - \text{Sr}(87/86)_{\text{init}}]$$

$\theta$  then replaces  $T$  as the vertical axis in the graph.

## *The Unmetamorphosed Granite*

In FIGURE 1 lines representing biotite, feldspar, and apatite from a granite together with a line for the granite total rock have been drawn on a graph with axes of age,  $T$ , and  $\text{Sr}(87/86)_{\text{init}}$ . In this case the granite is assumed to have remained unmetamorphosed since crystallization.

${}^*\text{Sr}^{87}$  = moles of radiogenic daughter strontium;  $\text{Rb}^{87}$  = moles of  $\text{Rb}^{87}$  now;  $\lambda$  = decay constant of  $\text{Rb}^{87}$ ;  $\text{Sr}^{86}$  = moles of  $\text{Sr}^{86}$  now;  $\text{Sr}(87/86)_{\text{now}}$  = total  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio now; and  $\text{Sr}(87/86)_{\text{initial}}$  = Initial  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio  $T$  years ago. (Sample assumed to form a closed chemical system at this instant.)





strontium is assumed to have been thoroughly mixed so that each mineral line must commence from the point of metamorphism defined by  $T_{\text{meta.}}$  and  $\text{Sr}(87/86)_{\text{meta.}}$ . It is assumed that the period of metamorphic activity is short compared with the time elapsed since the metamorphism. The total rock line will remain unaltered. The new mineral lines will have in general new gradients since the ratio common Sr/Rb alters at the time of the metamorphism.

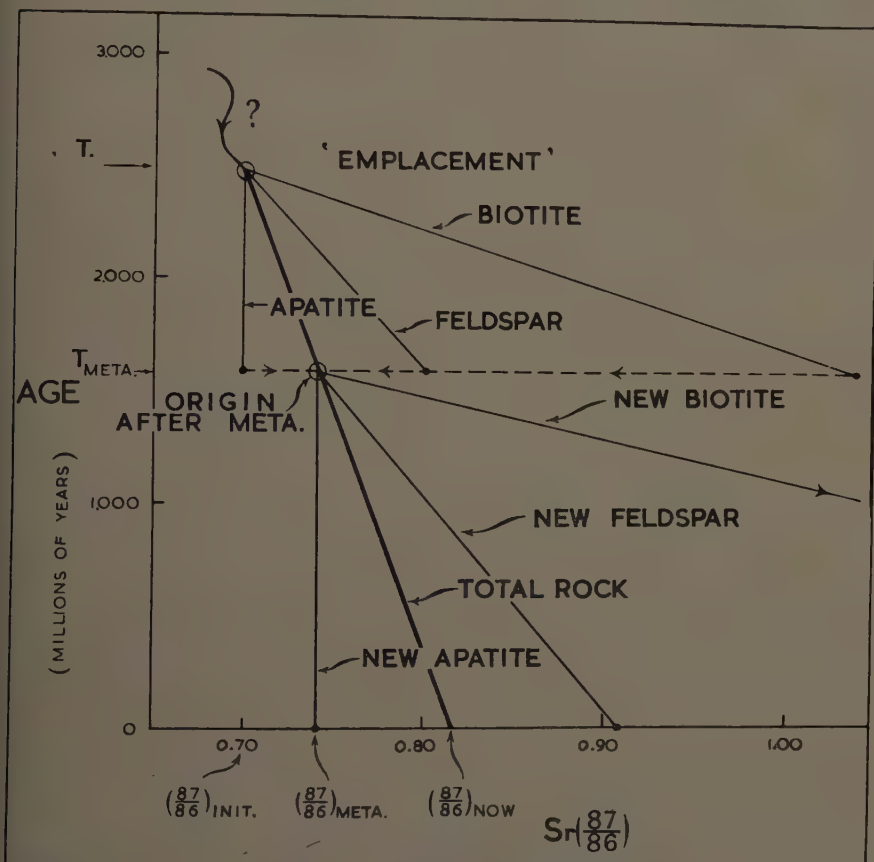


FIGURE 2. Metamorphosed granite.

ism. The age of the metamorphism is, however, completely defined by the intersection of the mineral and total rock lines.

In all cases a sample of the  $\text{Sr}(87/86)_{\text{meta.}}$  will be preserved in minerals containing little or no rubidium but rich in strontium. For a granite of high Rb/Sr ratio whose emplacement age is large compared with the time that has elapsed since its metamorphism the  $\text{Sr}(87/86)_{\text{meta.}}$  value will be much greater than that usually accepted for common Sr (0.71). Such a situation has been observed recently,<sup>2</sup> the presence of anomalous Sr being indicative of the metamorphism. For cases of this type the standard method of calculating mineral ages from Rb/Sr measurements will yield quite incorrect results.

*The Age of Emplacement*

The problem arises as to how the age of emplacement of a metamorphosed granite should be determined since the ages obtained from the mineral concentrates will probably be incorrect. The most conclusive evidence regarding emplacement age appears to be the concurrence of three or more granite total rock lines when each of the total rock samples has been taken from the one granite mass but, because of differing common Sr/Rb ratios, each has a different gradient.<sup>3</sup> No difficulty in selecting total rock samples with differing ratios has been experienced thus far, and any deviation from a single point of concurrence has been remarkably small.

When mineral concentrates are used, it has been found that each mineral may respond to metamorphism to a different degree so that a nonconcurrent series of ages will be observed. Muscovites seem to retain their original character through a mild metamorphism,<sup>3</sup> biotites however respond either partially or completely and should therefore be considered suspect in any attempt at absolute dating, while feldspars appear to be between these two extremes. There is some advantage to be gained from this variable response of different minerals since a mild degree of metamorphism will cause a biotite, for example, to respond either completely or partially while still leaving evidence of a previous strong metamorphism in other minerals.

*Conclusion*

By using a graphic method of representation for Rb-Sr data, it is possible to determine the crystallization age of a granite when three or more total rock samples are available.

One subsequent metamorphism may be dated under suitable circumstances by critically examining the age at which a mineral concentrate and a total rock sample have the same common strontium 87/86 ratio. If several samples of the one mineral all yield the same age under these conditions, it can be reasonably assumed that this age represents the time that has elapsed since the metamorphism. Under certain circumstances, due to the varying response to metamorphism of different mineral species, it may be possible to detect and date more than one period of metamorphism, although the errors involved under these circumstances are large.

This graphic approach to the dating of granites by the Rb-Sr method has been shown to yield a great deal of information that is not available from the raw data alone. In an ideal situation both the crystallization age and subsequent metamorphic history of a granite may be completely determined.

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*Discussion of the Paper*

S. R. HART (*Massachusetts Institute of Technology, Cambridge, Mass.*): Was mention made of finding some anomalous strontium in some apatites?

JEFFERY (*University of Western Australia, Nedlands, Australia*): Some anomalous strontium was found in an apatite; there was approximately 8 per cent enrichment in the  $\text{Sr}^{87}$ . It is believed this was essentially the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio at the time of metamorphism. Unfortunately, I did not see the Massachusetts Institute of Technology report until after I arrived in the United States or I should have altered this presentation.

In the apatite the anomalous strontium was formed during a metamorphism at 650 m.y. of a 2700-m.y.-old granite.

HART: Six hundred and fifty m.y. after emplacement?

JEFFERY: No, actually 650 m.y. ago.

L. T. ALDRICH (*Carnegie Institution of Washington, Washington, D.C.*): Was that determined by intersection of the total rock curve?

JEFFERY: We obtained approximately 20 intersections of biotite with different total rock lines for this 650-m.y. date. Biotites from many places in this granite have been taken to make sure that there is no error and there are innumerable intersections at about 650 m.y.

There are also some unexplainable intersections of epidote with total rock lines at about 1200 m.y., but the significance of these is unknown.

P. W. GAST (*University of Minnesota, Minneapolis, Minn.*): I have also found this in apatite. In apatite from one pegmatite that is very rich in rubidium, more than 50 per cent of the  $\text{Sr}^{87}$  was found to be radiogenic.

QUESTION: Was this believed to be metamorphism?

GAST: The problem was not followed far enough to establish a second metamorphism. Just this one measurement on it was made, and the pegmatite is another indication that there may be some recrystallization.

JEFFERY: I shall be cautious here because I am a physicist and have no desire to tread on any geologist's toes, but we had the samples of the granites that we used examined mineralogically *before* we started work on them. There was some indication of a low grade of metamorphism but not enough to suggest that the biotite had responded completely.

GAST: This agrees with your data. You have stated that the initial values in the granite are about 0.70. How certain is this value?

JEFFERY: Erring on the side of caution, the 0.70 could be 0.71 or 0.69, but I believe it is 0.70.

GAST: The strontium isotope composition on the meteorite analyzed by Schumacher has been redetermined along with a number of other basaltic achondrites and nothing lower than 0.700 was found.<sup>1</sup>

JEFFERY: Very interesting. This does not change the general pattern, but it will narrow down the permissible range indicated. The point 0.70 agreed nicely with Schumacher's value.

GAST: This has been redetermined several times. All of our measurements agree within two parts in 700. Two different meteorites, Nuevo-Laredo and Sioux County, also give values of 0.702 and 0.701.

JEFFERY: These figures change the data very little.

A. L. HALES (*Bernard Price Institute of Geophysical Research, University of Witwatersrand, Milner Park, Johannesburg, Union of South Africa*): Your diagram actually shows an intersection at the time the systems became independent chemical systems. Sometimes, under certain classical geological conceptions, this may not be the same time as the time of recrystallization. Caution must be used in choosing assemblages, that is, different rock types from which families of curves of this kind are prepared, or the things that might be used to give these curves.

JEFFERY: That is correct.

HALES: Perhaps it was implicit in your statement, but the time of separation of the system as a chemical system is not necessarily the time of crystallization and appearance in its present site.

JEFFERY: For anyone who is contemplating this approach, it is very important to make certain that the mineral concentrates worked on are part of the same type of rock sample, thoroughly mixed and quartered; otherwise completely erroneous results will be obtained.

HALES: When Deneys Schreiner started to work on the total rock procedure it was because he thought it possible that the individual minerals in a rock had not formed isolated systems since the time of their first emplacement. I am certain that he would be delighted to find this splendid verification of his original thought from a continent other than Africa.<sup>2</sup>

Since the time that the Bushveld paper was published, other measurements have been made. Nicolaysen speaks of some of them elsewhere in this monograph and I shall give information about the old rocks measured recently and present another example of total rock analysis using a slightly different mode of graphical presentation. Our conclusions are in general along the same lines as those of Jeffery and Compston (elsewhere in this monograph) with this exception: we are not absolutely certain that it is necessary to have a single time at which the strontium moves out of the biotite. There may also be a possibility that the strontium moves out of the biotite continuously throughout the history of the rock. With this one minor modification, the findings are generally in complete accord with those of Jeffery and Compston and we are very pleased to learn of it.

JEFFERY: The diagrams shown are completely idealized and your statement is quite correct, that is, that there may have been no single event that responded in the biotite, for example, and did not respond in the muscovite.

We feel that it was unfortunate that Schreiner did not, by sheer accident, look at a granite that had been strongly metamorphosed because all this would have been seen.

L. F. HERZOG (*Pennsylvania State University, University Park, Pa.*): My associates and I analyzed the same achondrite that Schumacher ran (actually before he did) and never obtained 87/86 below 0.697; his value was accepted as correct because he had a much better instrument with a bigger radius, triple-filament source, and multiplier collector.<sup>3</sup> Since then, however, it has been learned that there were some troubles connected with the electron multiplier-equipped instruments at Argonne, including the one Schumacher used. More-



over at a recent conference on uranium isotope measurements, some new information was presented by W. R. Shields of the Bureau of Standards, Washington, D.C. (unpublished observations) showing systematic differences between single filament and triple filament results. The measured isotope ratios could be compared for uranium against synthetic mixtures of pure  $U^{235}$  and  $U^{238}$ . I think that when the results of the uranium standardization program are final it will be possible to apply much of the knowledge developed to rubidium, strontium, and other isotope measurements also.

JEFFERY: Is vapor ionization or surface ionization used in these measurements?

HERZOG: We use surface ionization, both single and now triple filaments. A. O. Nier, I believe, used vapor ionization for his "standard" strontium measurement which, incidentally, agrees well with the single-filament measurement that Aldrich and I made in 1951.<sup>4</sup> May I ask Paul Gast how he got his 0.1186 value for  $Sr^{86}/Sr^{88}$ . It seems to me this has some bearing on the discussion.

GAST: It is essentially an arbitrary value. The only evidence I have for using it is that raw values in the range 0.1182 to 0.1190 turn up most frequently in those runs where there is no systematic change in the ratio during the run.

HERZOG: Our "best" value, which agrees with Nier's, is higher than that, much higher. What was your technique? What type of source or filament?

GAST: These measurements were made on a single filament, a tantalum filament; strontium perchlorate was the material initially used.

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## MINERAL AGES AND METAMORPHISM

Stanley R. Hart

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This paper reports the results of some investigations in progress at the Massachusetts Institute of Technology concerning the effects of metamorphism on mineral ages determined by the Rb-Sr and K-Ar methods.

The first topic concerns the redistribution of radiogenic strontium among the phases of a rock system during metamorphism. This investigation is being carried out by the M.I.T. group under the leadership of H. W. Fairbairn and was stimulated by a letter to *Nature* from W. Compston and P. M. Jeffery.\* The results Jeffery has discussed elsewhere in this monograph agree with those of the M.I.T. group, and I will cover this data only briefly.

The simplest model, shown schematically in FIGURE 1, assumes that the rock system is closed to rubidium and strontium and that complete isotopic equilibration of strontium has taken place at a time of metamorphism,  $t_m$ .

My associates and I have found two cases where biotite-feldspar-whole-rock growth lines intersect at common points, the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio at these intersections being 34 per cent and 10 per cent higher than the common strontium value of 0.712. This mutual intersection is evidence for the condition of complete isotopic equilibration of strontium and defines a time of metamorphism. The closed-system condition cannot be evaluated from these data, and whole rock ages can be calculated only by assuming some value for the initial  $\text{Sr}^{87}$  abundance. Several total rock samples from the same location would have to be analyzed, as Jeffery has done, to check this condition and obtain a definite whole-rock age.

It should be noted that use of the usual common strontium correction in calculating the mineral ages in the cases above leads to discordant ages, with the feldspar appearing older than the biotite. This older age for the feldspar is, in effect, imaginary and due to the lower Rb/Sr ratio in feldspar. It is not necessarily a function of better retention of radiogenic strontium in feldspar. Due to the high Rb/Sr ratio in the biotites above, an age calculated using the usual common strontium correction would give very nearly the true age of metamorphism.

Aside from the two cases described above, we have found one other case where a feldspar-whole-rock intersection occurs with 5 per cent radiogenic enrichment. The lack of a second mineral determination here prevents a test of the condition of complete strontium isotopic equilibration. Finally, there is a single case where the biotite-feldspar-whole-rock measurements do not intersect in a common point. One possible explanation for this is incomplete redistribution of radiogenic strontium at the time of metamorphism.

I shall change the subject somewhat now and discuss some preliminary results of a study of the measured ages across a contact zone between two Laramide intrusives and Pre-Cambrian country rock. This study is being carried

\* Compston, W. & P. M. Jeffery. 1959. Anomalous common Sr in granite. *Nature*. 184: 1792, 1793.

out near the Eldora and Audubon-Albion stocks in the Front Range, Colo., which cut Pre-Cambrian Silver Plume granite and sillimanite schists of the Idaho Springs formation. The contact metamorphism has caused very little macroscopic or microscopic change in the rocks. Thus far only K-Ar mineral ages have been determined; eventually the constituent minerals will also be analyzed for their Rb-Sr age.

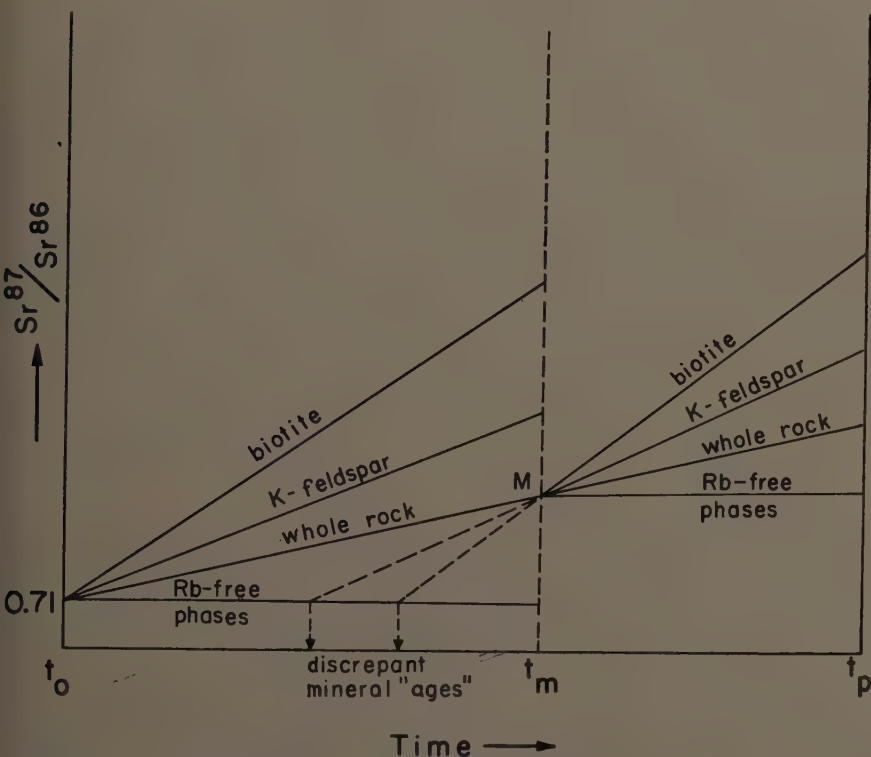


FIGURE 1. Schematic radiogenic growth curves for whole-rock and co-existing-mineral phases showing a metamorphic break in  $t_m$ . Closed system and complete recrystallization are assumed.

TABLE 1 shows the results for samples collected from the Idaho Springs formation near the Audubon-Albion stock. All the biotites, with one exception, give a similar age and serve only to date the time of intrusion at about 68 million years (m.y.). Additional samples will have to be collected at greater distances from the intrusive before any retention of argon in biotite is noticed. The one exception, with an age of 110 m.y., cannot be explained simply at this time.

The whole-rock Rb-Sr age of 900 m.y. at 46 m. distance is evidence that the size sample taken did not act as a closed system to rubidium and strontium during metamorphism. This is not surprising as the schist is not homogeneous on that scale. The 1700 m.y. whole-rock Rb-Sr age at 27 m. indicates either

that the Idaho Springs formation is at least 1700 m.y. old or that the sample inherited radiogenic strontium from the surrounding rocks at some time.

TABLE 2 contains results for samples taken in the Idaho Springs formation near the contact of the Eldora stock. One biotite shows the age of the intrusive, and the other shows slight retention of argon. The Eldora stock is smaller than the Audubon-Albion stock, so partial retention of argon at 76 m. is not inconsistent.

TABLE 1  
AUDUBON-ALBION CONTACT SAMPLES

Distance from contact (m.)	Biotite K-Ar age	Feldspar K-Ar age	Total-rock Rb-Sr age
Intrusive	69 $\pm$ 2		
12	68 $\pm$ 2		
27	110 $\pm$ 3	40 $\pm$ 2	1700 $\pm$ 100
46	69 $\pm$ 2		900 $\pm$ 50
91	67 $\pm$ 2		

TABLE 2  
ELDORA CONTACT SAMPLES

Distance from contact (m.)	Biotite K-Ar age	Hornblende K-Ar age
1.0		120 $\pm$ 4
3.5		950 $\pm$ 20
18.0	68 $\pm$ 2	
41.0		1160 $\pm$ 25
76.0	80 $\pm$ 2	1150 $\pm$ 25

TABLE 3  
MUSCOVITE FROM CLARENDON, VT.

Sieved grain size	Median radius (microns)	Measured K-Ar age
Hand picked, 2 mm.-1 cm.	>1000	700 $\pm$ 15
-10 + 20	690	555 $\pm$ 15
-28 + 40	250	440 $\pm$ 10
-50 + 100	110	350 $\pm$ 8
-100 + 200	55	360 $\pm$ 8

Hornblendes in the Eldora contact zone show remarkable argon retention when compared to the biotites. This difference is supported by laboratory measurements of the diffusion rate of argon in biotite and hornblende, with hornblende showing a diffusion coefficient about three orders of magnitude smaller than biotite. The laboratory diffusion studies were made by heating the minerals in vacuum. While the difference in diffusion coefficients measured for biotite and hornblende in this way is probably real, the absolute values are not geologically meaningful as these minerals in vacuum are unstable with respect to water loss.

The question of excess or inherited argon in amphiboles, raised by P. E.



Damon some years ago, must be settled before their high retentivity for argon can be utilized in geologic age studies.

It was hoped in these Colorado samples to be able to relate the amount of argon loss in biotite to grain size, but none of the samples show sufficient argon retention for such a study. However, a sample of muscovite-bearing marble collected from a Pre-Cambrian area in Vermont by W. H. Pinson of the Massachusetts Institute of Technology has been utilized for a grain size study. TABLE 3 shows the measured K-Ar ages for various size fractions of muscovite separated from this marble. The marble sample was crushed and ground in a routine way before screening; it is possible that some of the muscovite has been reduced. The listed grain sizes are therefore only minimum values. Hopefully, the relatively soft marble did not cause much pulverizing of the muscovite.

The two smallest grain sizes show the same age, and this can be interpreted as being the age of metamorphism. The coarser sizes show progressively greater ages, the coarsest size still showing about 50 per cent loss if the muscovite is assumed to be of Grenville age initially.

It is clear that a single age on a sample such as this is geologically meaningless, in an absolute sense. However, by analyzing several size fractions, an age of metamorphism can be established, and also an indication that the original age is much greater. In future work on mixed-age areas, grain size must be considered and should be recorded.

#### *Discussion of the Paper*

P. E. DAMON (*University of Arizona, Tucson, Ariz.*): My associates and I measured some hornblende from the Storm King pegmatite and obtained an age of 1400 m.y., while a biotite gave an argon age of 900 m.y. We ascribe this, possibly, to initial argon because, as is known, the alkali-cation position is not completely occupied in hornblende. In tremolite, where the alkali-cation position is completely vacant, investigation of the K-Ar age might settle this problem.

HART: This is something that should have a little more investigation. Results on the Storm King may have discouraged everyone from using hornblendes. Most hornblendes carry enough potassium to date by present techniques and it is possible that even pyroxenes can be used. Both of these may show higher retention of argon under metamorphic conditions than biotite.

One age has been done on a hornblende from Chicoutimi, Quebec, which had a 950 m.y. Rb-Sr age, and the argon age was approximately 900 m.y. Thus far I have found no argon ages on hornblendes that suggest excess argon.

QUESTION: Did you ever look at helium in the hornblende from the Storm King?

DAMON: Yes, we also investigated helium in this particular hornblende, but found no excess.

P. M. JEFFERY (*University of Western Australia, Nedlands, Australia*): Have you done any K-Ar ages on the samples for which you did the Rb-Sr work?

HART: Yes, in almost all cases there are K-Ar ages on the biotites.

JEFFERY: What about the granites?

HART: There is usually marked disagreement between the biotite-argon ages, and the whole-rock strontium ages. Most of the results mentioned are from the Sudbury, Ontario area, and it is a considerably mixed-up area.

L. T. SILVER (*California Institute of Technology, Pasadena, Calif.*): This general comment is made after thinking about the geologic implications of much of the discussion presented thus far. I am somewhat puzzled. After seeing the analyses of granites reported by P. W. Gast, it would appear that correction can be made back to the original strontium in each of these cases and that they are essentially of the same composition. However it is possible that the classical geological processes, characterized in FIGURE 1 as complete metamorphism, be characterized as the development of a magma, and as a magma of a composition similar to that of some of the rocks analyzed by Gast.

Complete metamorphism of a rock producing, for example, any low-temperature melting fraction from a rock that has developed a characteristic radiogenic rock strontium should, to my mind, still give the same radiogenic rock strontium or something certainly radiogenic to some degree and characteristic of the environment in which it is developing. I am somewhat confused by the fact that in these rocks showing, for example, a good granite composition that might well be developed from a low melting fraction of the crust, more evidence is not found of this radiogenic "common" strontium. To my way of thinking that is about the only case now with the definite condition of complete metamorphism. Otherwise, there is some concern about the specification of these conditions of complete metamorphism.

HART: Measurements on individual minerals and on the whole rock are needed. A mutual intersection is strong evidence for isotopic equilibration of strontium, and certainly this can be accomplished without melting.

SILVER: If a magma is used initially that has radiogenic strontium, then there is only one cycle, not the 2-cycle stage. That might be called metamorphism, but it is still magmatism, and that is the last episode.

JEFFERY: All that is necessary here is the condition of solid state diffusion rather than complete metamorphism.

SILVER: I agree. We are talking fundamentally here about homogenization of a system at this time regardless of what mechanism is used, but this should be correlated with geological phenomena. The geologist is put on the spot when he is handed a specimen and asked what he can see in it. There might be a good reason why he does not see evidence of the effects found and, although as a geologist I attempt to be aware of the matters under discussion here, I still must regard those parameters I have been using for a long time.

JEFFERY: In the cases observed, there has not been complete homogenization.

HART: In our case, the homogenization is not necessarily reflected in any visible parameters in the rock. In the Colorado rocks, homogenization of strontium, as well as loss of argon, has taken place, but there is no visual evidence of this in thin sections of the samples.

SILVER: Nevertheless the samples were picked up in one of the most profoundly mineralized zones in the Colorado Rockies. Thus the question is whether the homogenization of K-Ar ages reflects the contact metamorphism

or some other effect, namely, hydrothermal mineralization in the porphyry belt.

L. F. HERZOG (*Pennsylvania State University, University Park, Pa.*):  $\text{Sr}^{87}/\text{Sr}^{86} = 0.712$  was used uniformly to obtain discordant ages; is that correct? There is an intersection somewhere above this line. In the rocks were any rubidium-free minerals measured?

HART: No, we have not done this yet. This is something we intend to do using, for example, apatite or fluorite.

P. M. HURLEY (*Massachusetts Institute of Technology, Cambridge, Mass.*): This is a highly selected set of data. The Sudbury area is known to have suffered metamorphism at the time of the Grenville and at the time of emplacement of the norite. Both of these effects are superimposed on an ancient cratonic mass that presumably had an age of about 2500 m.y. If relatively young intrusives were to be selected, such as plutonic granites of batholithic dimensions found in Nova Scotia and British Columbia, I believe that all of the initial strontium 87 intersections for the different minerals would occur close to the 0.712 value and show that these materials had appeared at the earth's surface from below the crust at the time of their emplacement, as opposed to being reworked older sialic material, in which the initial strontium 87 abundance would be higher than 0.712. Most of the cases selected by Gast suggest granites that were not formed by the reworking of more ancient sialic material. These thoughts can be applied to the Colorado results.

P. W. GAST (*University of Minnesota, Minneapolis, Minn.*): May I ask if there is any evidence that there is differential movement between the radiogenic strontium and the normal strontium in these minerals?

HART: No, there is not. The radiogenic strontium may occupy a different position from the common strontium, in which case it might very well move differently. This could be tested by heating a sample of granite and measuring it.

JEFFERY: We have done nothing in this connection, but we have assumed, of course, that the radiogenic strontium does not move differentially.

L. T. ALDRICH (*Carnegie Institution of Washington, Washington, D.C.*): My associates and I have just one measurement on a muscovite that is intergrown, at a later time than the time of metamorphism of a slate. This is a fairly complex environment, but the petrologists have assured me that the muscovite could not have been formed at the time of the biotite because of the high metamorphic grade of the slate. The K-Ar age of the muscovite was definitely younger than the K-Ar age of the biotite intergrown with it. However, it appeared that the strontium was so very common that it could not have come from the biotite surrounding it.

# GRAPHIC INTERPRETATION OF DISCORDANT AGE MEASUREMENTS ON METAMORPHIC ROCKS

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The first systematic age measurements based on the decay  $\text{Rb}^{87} \rightarrow \text{Sr}^{87}$  were largely carried out on pegmatites and massive granites, and the ages obtained for coexisting mica and K-feldspar in these rocks were usually in good agreement (Aldrich and Wetherill, 1958, Table VIII). Recently published age measurements on certain metamorphic rocks of granitic composition have disclosed the following important feature: gross discordance between the mica age and the K-feldspar age (with the mica age very much less than the feldspar age) when these ages are calculated according to the following assumptions:

(1) There have been no changes in the content of  $\text{Rb}^{87}$  and  $\text{Sr}^{87}$  in the mineral since the time of formation except for the nuclear transformations.

(2) The content of nonradiogenic  $\text{Sr}^{87}$  in the mineral can be estimated by taking 0.71 times the measured proportion of  $\text{Sr}^{86}$  or 0.084 times the measured proportion of  $\text{Sr}^{88}$ ; these factors result from the many Sr isotopic abundance measurements on terrestrial minerals with high Sr/Rb ratios, which show constant values to within a few per cent and indicate that any world-wide increase in the  $\text{Sr}^{87}$  abundance over geological time has been less than 2 per cent. It is therefore assumed that the Sr incorporated in the mineral at the time of formation was typical of this world-wide "pool" of common strontium.

For the gneiss of the Baltimore, Md., area, Tilton *et al.* (1958) thus reported the presence of  $\sim 300$  million-year (m.y.)-old biotite in the form of unstrained crystals coexisting with  $\sim 1160$  m.y.-old K-feldspar in the form of irregular shaped microclines having delicate projections and interlocking contacts with other minerals. They conclude that the microcline and zircon probably record a 1000 to 1100 m.y.-old crystallization, while biotite records a second crystallization 300 to 350 m.y. ago.

Compston and Jeffery (1959) presented certain data for the Boya granite near Perth, Australia, indicating the coexistence of a 650 m.y.-old biotite and a 1290 m.y.-old microcline, if these assumptions are employed. However, these authors presented a graph of the assumed  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in the nonradiogenic component versus a parameter proportional to the calculated age. This plot showed that the biotite, microcline, and total rock samples give a concordant age close to 520 m.y. if the value 0.82 is used for the  $\text{Sr}^{87}/\text{Sr}^{86}$  of the primary component; the presence of anomalous  $\text{Sr}^{87}/\text{Sr}^{86}$  (with a ratio 0.77) was also reported for the apatite and epidote in this rock. The interpretation of these authors is that the granite crystallized at least 2400 m.y. ago, but was metamorphosed at about 520 m.y. ago. During this metamorphism the rock is believed to have remained a closed system.

My associates and I have studied the granite occurring 3 miles northeast of Mbabane in the Swaziland Protectorate in Africa. This granite is termed

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"G5" in the Swaziland granite classification of Hunter. It shows the same general pattern when the above-mentioned assumptions are used. The total-rock sample and the sample of quartz plus total feldspar show ages close to 2600 m.y., the idiomorphic sphene crystals have a  $\text{Pb}^{207}\text{-Pb}^{206}$  age close to 2700 m.y., but two micaceous samples, consisting of purified biotite and chloritized biotite respectively, show ages of  $\sim 1950$  m.y.

L. T. Silver reported elsewhere in this monograph that measurements on metamorphics are now taking us on a new avenue toward some of the fundamental questions of petrogenesis. We fully endorse this optimistic approach. For example, if the Boya granite had shown apatite and epidote with  $\text{Sr}^{87}/\text{Sr}^{86}$  values equal to 0.82, this would have been an indication of an intense metamorphic process with very high effective mobility as far as the strontium is concerned. We now have the tools for distinguishing between times of formation of heterogeneous chemical systems and times of partial and total fusion, and particularly for distinguishing between certain paragneisses and orthogneisses.

An important question that should challenge all workers in this field concerns the most fruitful and unambiguous way of displaying and analyzing the Rb-Sr analytical data on such metamorphic rocks. A plot of the parameters  $\text{Sr}^{87}/\text{Sr}^{86}$  versus  $\text{Rb}^{87}/\text{Sr}^{86}$  (both expressed as atomic ratios) has certain advantages: (1) for most K-feldspars and total rocks and for many metamorphic micas, the  $\text{Sr}^{87}$  and  $\text{Sr}^{86}$  isotopes are of approximately the same proportion, and their ratio can be measured rather precisely (standard deviation  $< 0.5$  per cent); and (2) this plot is amenable to study of the effect of relative movements of the two elements rubidium and strontium within the various minerals and rocks.

As FIGURE 1 indicates, any age calculation on a mineral or rock (represented by the point marked 1) consists effectively of drawing a line between 1 and a point on the vertical axis (representing the primary strontium isotope ratio in the mineral at the time of its formation); the slope of this line, that is,  $\tan \alpha = (\Delta\text{Sr}^{87}/\Delta\text{Rb}^{87})$  is measured and substituted into the age equation:

$$t \text{ calculated} = \frac{\ln (1 + \tan \alpha)}{\lambda},$$

where  $\lambda$  is the decay constant of  $\text{Rb}^{87}$ .

An age may also be obtained by drawing a line between mineral component 1 and another mineral component 2 if we make the assumption that these two minerals formed at the same time and incorporated primary strontium of identical isotopic composition, represented by the point 0. In both cases we still make the assumption referred to earlier, that is, that no fractionation of strontium or rubidium has taken place in any of the minerals since their formation. FIGURE 2 illustrates a graph of this nature.

Examples of this type of plot are given in FIGURE 3 for the Mbabane (Swaziland G5) granite and in FIGURES 4 and 5 for the Baltimore gneiss data given by Tilton *et al.* (1958). The Towson, Phoenix, and Woodstock domelike occurrences of this gneiss are situated about 12 miles from each other. Tilton *et al.* have specifically interpreted the data on the Towson microcline as indi-

cating that the strontium incorporated in the Phoenix microcline was similar to "common strontium" in its isotopic composition, in spite of the considerable distance between the rock samples.

One feature is common to the three areas: the feldspar and biotite samples have concordant ages if a particular "anomalous" and high value of the  $\text{Sr}^{87}/\text{Sr}^{86}$

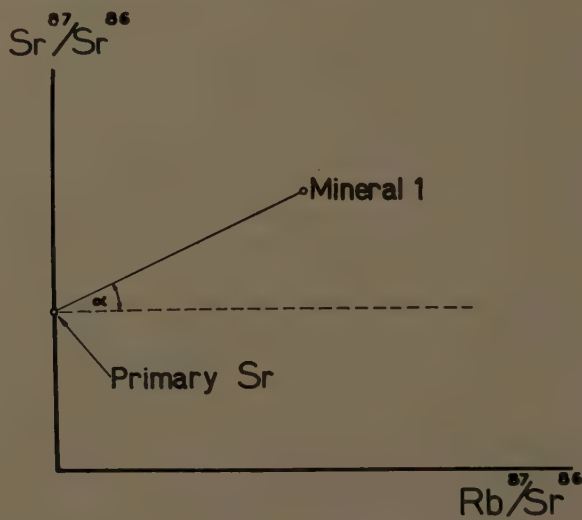


FIGURE 1. Correction for nonradiogenic strontium.

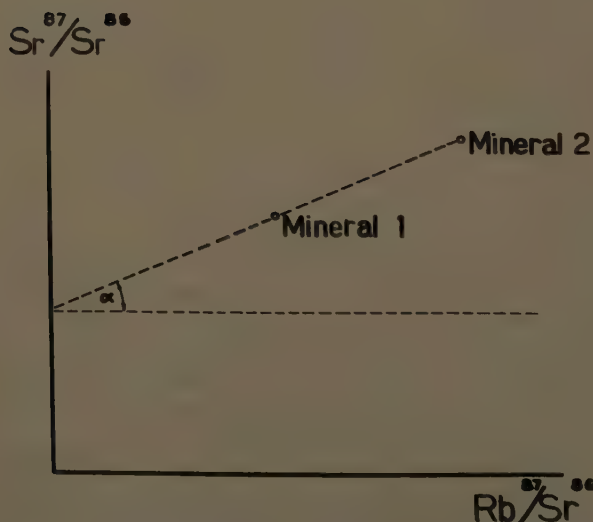


FIGURE 2. Use of a mineral pair for establishing the nonradiogenic strontium component.

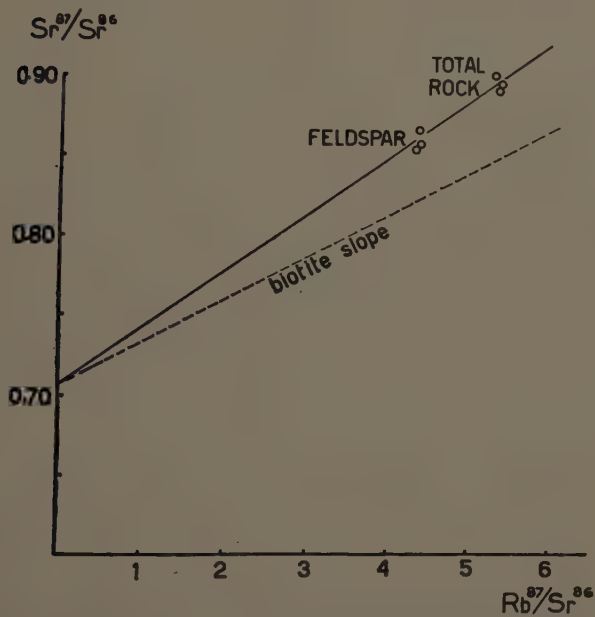


FIGURE 3. Isotopic analyses of the granite northeast of Mbabane, Swaziland Protectorate, Africa.

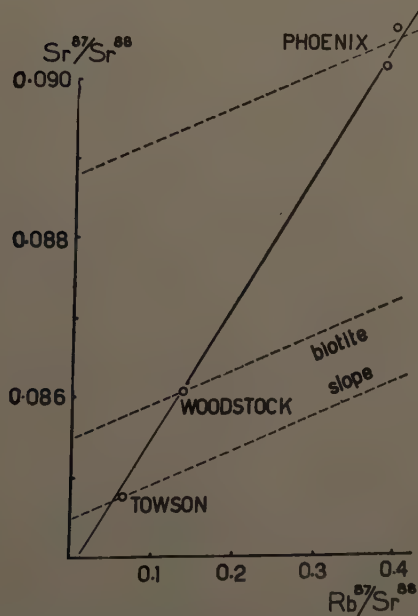


FIGURE 4. Isotopic analyses of microclines from various domes of the Baltimore gneiss.

or  $\text{Sr}^{87}/\text{Sr}^{88}$  ratio is used for the nonradiogenic component as:

	Northeast of Mbabane	Phoenix Dome	Boya granite
"Concordant" age using anomalous strontium	$\sim 1950$	$\sim 300$	$\sim 520$
Isotope ratio of the anomalous strontium	$\text{Sr}^{87}/\text{Sr}^{86} = 0.75$	$\text{Sr}^{87}/\text{Sr}^{88} = 0.089$	$\text{Sr}^{87}/\text{Sr}^{86} = 0.82$

This relationship is shown by the lines of lesser slope in FIGURE 4, the extension of straight lines joining the microcline and biotite points; if the bulk of the rubidium and strontium in the Phoenix Dome sample is contained in this pair of minerals, the "total-rock" point will fall close to the same line and the same type of "triple concordance" (shown for the Boya granite) will hold.

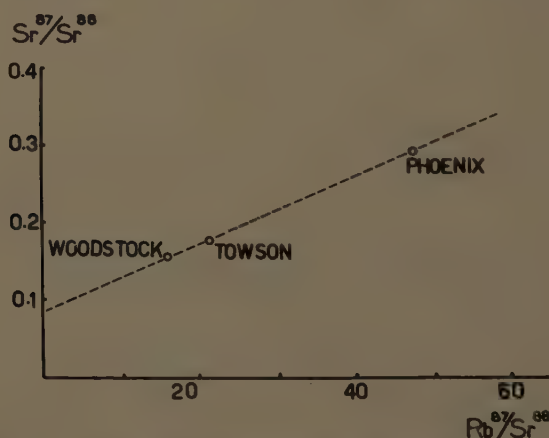


FIGURE 5. Isotopic analyses of biotites from the Baltimore gneiss.

Several questions arise from an examination of the data for the Swaziland granite G5, the Boya granite, and the Baltimore gneiss:

(1) What critical evidence would indicate whether the feldspar has remained a closed system with respect to rubidium and strontium, or whether the metamorphism was intense enough to bring about an isotopic mixing of the strontium in all phases present so that it would be justifiable to speak of the microcline having an "age" of  $\sim 1950$  m.y. (Mbabane) or  $\sim 300$  m.y. (Phoenix Dome)?

(2) What was the destiny of the radiogenic  $\text{Sr}^{87}$  generated in biotite between the original crystallization of the rock and the time of metamorphism? This information may help to distinguish between micas that have suffered complete and incomplete expulsion of strontium during metamorphism.

(3) Did the particular whole-rock sample behave as a closed system or an open system with respect to rubidium and strontium during metamorphism?



Concerning the first question: it may be suggested for example, that further analyses of feldspar samples from different localities of the Baltimore gneiss may yield points that continue to lie along the steeper line in FIGURE 4; this would be very strong evidence that these feldspars all crystallized with an identical strontium as a primary component and that each feldspar has remained as a closed chemical system (with respect to rubidium and strontium), although there may have been slight changes in physical morphology. The slope of the line (equivalent to  $\sim 1100$  m.y.) would date the time of formation of the family of related microclines as a heterogenous chemical system. If isotopic mixing has taken place during metamorphism, these points would not be expected to have this regularity, and the presence of anomalously high  $\text{Sr}^{87}/\text{Sr}^{88}$  ratios in the apatite and epidote of these rocks would be predicted. As shown in FIGURE 4, the presence of rather different strontium isotopic compositions for the apatites of the Phoenix, Woodstock, and Towson domes would be expected.

As a first step towards understanding the next problem, consider a simplified granite in which just two phases (mineral 1 and mineral 2) contain the bulk of the rubidium and strontium in the rock. Let  $p_1$  and  $p_2$  be the weight proportions of these two minerals in the rock. Assume Rb and Sr are always present in sufficiently small proportions so that  $p_1$  and  $p_2$  are not affected by transfers of these elements. Consider internal fractionations alone, and that any Sr lost from phase 2 (for example, biotite) was gained by phase 1 (for example, total feldspar).

Let  $R_1$ ,  $R_2$  be their respective contents of  $\text{Rb}^{87}$

$A_1$ ,  $A_2$  be their respective contents of  $\text{Sr}^{87}$

$S_1$ ,  $S_2$  be their respective contents of  $\text{Sr}^{86}$

at the instant before metamorphism. During metamorphism the points for mineral 1 and mineral 2 will move in a manner similar to that shown in FIGURE 6a. The positions of the mineral fractions at the following times are indicated by subscripts, noted here in parentheses: time of rock formation(s), instant before metamorphism (m), instant after metamorphism (n), and present day (measured). Mineral ages small compared to the half life of  $\text{Rb}^{87}$  ( $\sim 50 \times 10^9$  yrs.) are illustrated; in this case the very slight curvature of the vertical "growth-lines" in FIGURE 6 can be neglected.

The following relations are clear:

(1) After any fractionations the points for 1, 2, and the total rock continue to lie on a straight line and will also lie on a straight line when measured at any particular time after the metamorphism.

(2) If only Rb moves between the two phases during metamorphism, the lengths of the vectors ( $V_1$  and  $V_2$ ) describing the movement of each point have the relation  $V_1 p_1 S_1 = V_2 p_2 S_2$ .

(3) If only  $\text{Sr}^*$  moves (from phase 2 to phase 1) during metamorphism, as in FIGURE 6a, and the  $\text{Sr}^{87}$  content of 2 declines from  $A_2$  to  $(A_2 - q)$ , then the hori-

\* This Sr is assumed to be a representative sample of the Sr in the biotite at the time of metamorphism.

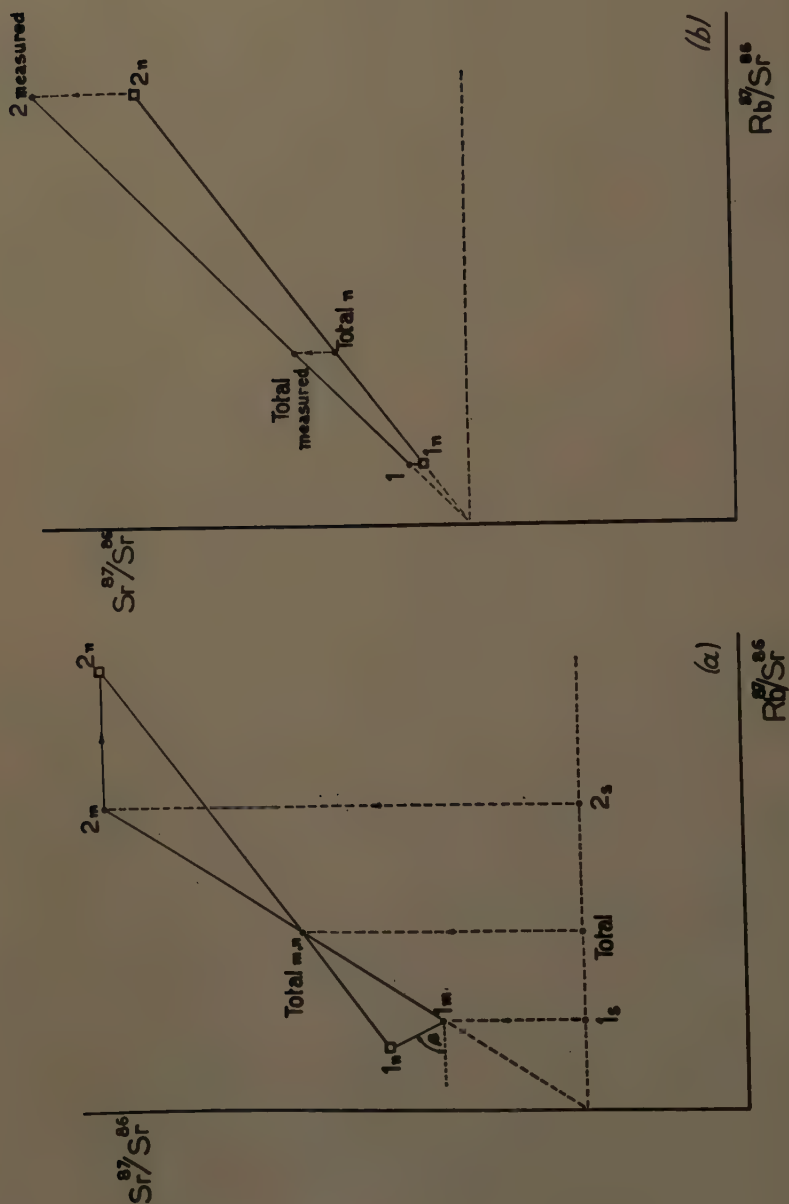


FIGURE 6. (a) Growth histories of the mineral pair from initial crystallization to the time of metamorphism and during metamorphism. (b) Growth histories of the mineral pair after metamorphism.

zontal vector describing the movement of 2 has a length  $(R_2/S_2)[q/(A_2 - q)]$ , and the direction of movement of 1 is defined by

$$\tan \beta = \frac{S_1 A_2 - S_2 A_1}{R_1 S_2}$$

that is, a function independent of  $q$ ,  $p_1$ , or  $p_2$ .

Consider any metamorphosed granite in which there is a close approximation to a two-phase distribution of most of the rubidium and strontium, for example, some granites containing microcline microperthite and biotite; there will always be a "triple concordance" of the ages of the microcline, total rock and biotite, with a particular value of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio used for the primary strontium component. However, as Compston and Jeffery have noted elsewhere in this monograph, taking this as the age of the metamorphic impress on the minerals is justified only if there was complete mixing of the strontium isotopes between the minerals during metamorphism. If there was merely a partial transfer of strontium from the biotite to the microcline, *then this "triply concordant" age would certainly overestimate the age of the metamorphism.* This possibility is clarified in FIGURE 6b.

When the bulk of the rubidium and strontium in the rock is contained in the two minerals plotted and there is a strong possibility that one phase (for example, feldspar) acted as a "soak" for strontium expelled from the other phase (for example, biotite), there is a particular need for caution in interpreting the data.

An application of the graphical procedure of FIGURE 2 occurs where a uniform biotite-bearing igneous rock has been metamorphosed. An array of points are plotted for two fractions, biotite and "the rest", as successively higher metamorphism is attained. For internal transfers the slopes of the lines (between the two fractions) are precisely defined by certain simple relationships between the weight proportion of biotite, the rubidium and strontium contents of the fractions, and the times of initial crystallization and metamorphism.

If good independent evidence is available (for example, from U-Th-Pb minerals) concerning the time of initial crystallization of a rock and the time of a subsequent metamorphism, this information imposes useful restraints on the interpretation of the Rb-Sr data. In particular, it allows a distinction between different ways in which expulsion of radiogenic  $\text{Sr}^{87}$  from the mica could have occurred.

### *Equivalent Graphs for the Uranium-Lead System*

The axes in the graphs referred to may be transformed to  $\text{U}^{238}/\text{Pb}^{204}$  versus  $\text{Pb}^{206}/\text{Pb}^{204}$ . This plot is useful for study of fractionations in U and Th minerals. Consider a large uniform crystal of such a mineral, that has been subjected to chemical alteration in recent times. If several portions of the crystal are analyzed, the relative movement of the chemical components will be manifested in a distinct pattern of discordant Pb-U ages for each fraction. These data will give rise to an array of points on the graph of  $\text{U}^{238}/\text{Pb}^{204}$  versus  $\text{Pb}^{206}/\text{Pb}^{204}$ . The horizontal or vertical alignment of this array can allow a significant distinction between discordant ages due to: (1) movement of ura-

nium with respect to primary lead; and (2) movement of radiogenic lead with respect to primary lead.

To assist in the interpretation of discordant age measurements it is important that workers should publish their detailed strontium or lead isotopic data in "raw" form. It is preferable to quote the strontium data as " $\text{Sr}^{87}/\text{Sr}^{86}$ " or " $\text{Sr}^{87}/\text{Sr}^{88}$ " in the mineral or rock sample, instead of "per cent radiogenic Sr." Modal analyses are very relevant to interpretation of the data.

### *Acknowledgment*

The experimental data on the Swaziland granite occurring northeast of Mbabane were obtained in a joint investigation with my colleague A. J. Burger, to whom I am also indebted for fruitful discussions.

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## ANALYSES OF IDENTICAL SAMPLES BY MORE THAN ONE LABORATORY\*

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In the early days of radioactivity-age determination, relative numerical "ages" comparable in accuracy with those that could be obtained through the use of the fossil time scale were considered satisfactory. However as time has gone on and techniques have improved, age-determination methods have been asked to give results of greater and greater precision.

The reason for this demand for greater accuracy is obvious when we consider that a stated uncertainty of  $\pm 5$  per cent in age (today considered very good work indeed) means, in the case of a one-billion-year-old sample, an uncertainty of 100 million years (m.y.): that is, a period of time comparable in length to the entire Tertiary period.

Aside from the problem of eliminating the uncertainties in age that result from uncertainties in decay constants, there is the question: How accurate are the methods presently used for the quantitative determination of the concentrations of parent and daughter nuclides? Thus far there have been very few studies made in which investigators at several laboratories, all using a single method, have analyzed identical samples, and there are even fewer cases wherein investigators using different analytical techniques have worked on identical samples. Cases where several independently collected samples taken from a single mineral deposit have been analyzed by more than one group are somewhat more numerous and thus are also of considerable present interest as evidence in regard to analytical accuracy, at least as regards age. However they are necessarily less informative even here than studies of identical samples, as it is not yet known in any particular case how to select samples that should in fact be expected to give identical ages.

I have been asked to summarize one recent study in which several laboratories analyzed the same samples. The specimens analyzed were all lepidolites, and the elements and their isotopes determined were rubidium and strontium. The analytical techniques used thus far have included mass spectrometric stable isotope dilution (MSID), optical emission spectrography (OS), neutron activation (NA), and X-ray fluorescence (XRF).

At the suggestion of Louis Ahrens, who was then at the Massachusetts Institute of Technology, Cambridge, Mass., Milo Backus ground up and purified to varying degrees five samples of lepidolite having various ages; after homogenizing each sample, he prepared individual aliquots by accepted techniques and shipped a set of five aliquots to each of several laboratories that had indicated an interest in this class of analysis. Inadvertently, all of the aliquots prepared were shipped, hence the analyses at the Massachusetts Institute of Technology had to be made on portions of the residual bulk samples.

\* Contribution 60-5, College of Mineral Industries, The Pennsylvania State University, State College, Pa.

Thus far several of these "intercomparison suite lepidolites" have been analyzed as follows:

For both strontium and rubidium, by stable isotope dilution, (1) at the Department of Terrestrial Magnetism of the Carnegie Institution, Washington, D.C.,<sup>1</sup> all five samples, some in replicate; (2) at the Enrico Fermi Institute of the University of Chicago, Chicago, Ill. (preparation) and at the Argonne National Laboratory, Lemont, Ill. (mass spectrometry) by E. Shumacher, one sample reported (personal communication); (3) at the United Kingdom Atomic Energy Establishment at Harwell, England, by R. K. Webster *et al.*, two samples;<sup>2</sup> and (4) at the Massachusetts Institute of Technology by my associates there and myself, all five samples.<sup>3</sup>

For rubidium only, by neutron activation by R. K. Webster *et al.*,<sup>2</sup> Atomic Energy Research Establishment, Harwell, England;

For Rb/Sr ratio, by X-ray fluorescence by my students and myself at The Pennsylvania State University, University Park, Pa. (unpublished observations);<sup>4</sup>

In addition, some of the gross samples from which the calibration suite mentioned above was prepared had already been analyzed for Rb/Sr and, in some cases, for Rb and Sr concentration by optical emission spectrography by Ahrens and his students, primarily during the period that he was at the Massachusetts Institute of Technology.<sup>5-8</sup>

Herzog *et al.*<sup>3</sup> have summarized and discussed the isotope-dilution determinations and referred also to the NA and OS work; accordingly I shall not dwell on these at this time. The earliest of the X-ray fluorescence work has also been reported by myself;<sup>4</sup> my associates and I have, however, done some additional X-ray work since that time, using a different type of detector, and I have included this work also in this report.

#### ISOTOPE DILUTION INTERCOMPARISONS

For MSID a standard solution and one or more "spike" (enriched isotope tracer) solutions calibrated against it must be prepared for each element to be studied. Furthermore, a single "age" determination requires two concentration determinations: one for parent nuclide and one for daughter (for example, Rb<sup>87</sup> and Sr<sup>87</sup> in the present case) and, ordinarily (but not for lepidolites), a careful isotope-ratio analysis of the daughter element.

For the analyses reported in these tables each laboratory prepared its own standard and spike solutions. In addition, at the Massachusetts Institute of Technology at least, more than one spike preparation per element was used because the original solutions were used up during the course of the investigation, which extended over many months.

In view of the number of operations involved in an Rb-Sr age determination—sample decomposition, "spiking," ion-exchange chemistry, and mass spectrometric analysis—the very small ranges displayed by the ages reported by the several investigators for samples from particular localities (in TABLES 1 and 2) is evidence that isotope dilution is an analytical technique indeed capable of high accuracy.

TABLE 1  
RUBIDIUM AND STRONTIUM CONCENTRATIONS:  $Rb^{87}/Sr^{87}$  RATIOS AND AGES REPORTED FROM FOUR LABORATORIES  
FOR AN INTERCOMPARISON SUITE OF FIVE LEPIDOLITES

Sample	Laboratory*	$Rb^{87}$ (ppm)	Radiogenic $Sr^{87}$ (ppm)	Normal $Sr$ (ppm)	$Sr^{87}/Rb^{87}$ ( $\times 10^6$ )	Age ( $10^8$ yr units)	Average book diameter (mm.)
L-N45 Bikita Quarry, Southern Rhodesia	MIT DTM INS HAR HAR	9170 $\pm$ 150 9350 $\pm$ 100 8930 $\pm$ 250 9320 9400	329 $\pm$ 6 356 $\pm$ 6 349 $\pm$ 10 346 342	<1.9	3590 $\pm$ 130 3800 $\pm$ 100 3910 $\pm$ 215 3710 3630	2530 $\pm$ 90 2690 $\pm$ 70 2760 $\pm$ 150 2630 2570	0.15
Average		9235	344.5		3730	2635	
L-A106 Bob Ingersoll Mine, S.D.	MIT DTM DTM DTM	3505 $\pm$ 53 3280 $\pm$ 60 3480 $\pm$ 60 3410 $\pm$ 60	80.1 $\pm$ 2 75.8 $\pm$ 2.0 81.6 $\pm$ 2.0 84.7 $\pm$ 2.0	<0.2	2290 $\pm$ 110 2320 $\pm$ 70 2360 $\pm$ 70 2480 $\pm$ 70	1630 $\pm$ 80 1655 $\pm$ 50 1680 $\pm$ 50 1770 $\pm$ 50	1.5
L-A107 Pala Mine, Southern Calif.	MIT DTM HAR HAR	3870 $\pm$ 80 4980 $\pm$ 55 4960 4810	6.45 $\pm$ 0.60 7.38 $\pm$ 0.10 6.9 7.0	0.58	167 $\pm$ 21 148 $\pm$ 5 139 146	120 $\pm$ 15 107 $\pm$ 4 100 105	0.3
L-A109 Southeast Manitoba, Canada	MIT DTM	5880 $\pm$ 90 6240 $\pm$ 60	191 $\pm$ 13 236 $\pm$ 5	0.5	3250 $\pm$ 300 3800 $\pm$ 100	2300 $\pm$ 230 2690 $\pm$ 80	0.5
L-A110 Varutrask, Sweden	MIT DTM DTM	5140 $\pm$ 110 5810 $\pm$ 120 5810 $\pm$ 60	128 $\pm$ 6 144 $\pm$ 2 144 $\pm$ 2	3.9	2490 $\pm$ 200 2510 $\pm$ 70 2510 $\pm$ 70	1775 $\pm$ 140 1790 $\pm$ 60 1790 $\pm$ 60	10.0

\* MIT, Massachusetts Institute of Technology, Department of Geology and Geophysics, Cambridge, Mass.;<sup>3</sup> DTM, Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, D.C.;<sup>1</sup> INS, Institute of Nuclear Studies, University of Chicago, Chicago, Ill. (E. Schumacher, personal communication); HAR, United Kingdom Atomic Energy Establishment, Harwell, England.<sup>2</sup> See text and references for further details.

TABLE 2  
COMPARISON OF STABLE-ISOTOPE-DILUTION ANALYSES OF INDEPENDENTLY  
COLLECTED SAMPLES FROM PARTICULAR LOCALITIES

Sample	Laboratory*	Rb <sup>87</sup> (ppm)	Sr <sup>87</sup> (ppm)	Sr <sup>87</sup> /Rb <sup>87</sup> (× 10 <sup>3</sup> )	Reference
Bikita District, Southern Rhodesia					
1 (L-N45)	MIT	9170	329	3590	3
(L-N45)	DTM	9350	356	3800	1
(L-N45)	INS	8930	349	3910	Schumacher (personal communication)
(L-N45)	HAR	9360†	344†	3670†	2
2	DTM	8750	330	3770	12, 13
Ranges		7.1%	7.9%	7.3%	
Bob Ingersoll Mine, South Dakota					
1 (L-A106)	MIT	3505	80.1	2290	3
(L-A106)	DTM	3390†	80.7†	2390†	1
2	McM	4490§	73.5	1640§	15
3	DTM	3380	73.5	2170	1
4	DTM	3255†	73.0†	2245	11
Ranges		7.4%§	10.0%	9.6%§	
Pala Mine, San Diego County, Calif.					
1 (L-A105)	MIT	3870	6.45	167	3
(L-A105)	DTM	4980	7.38	148	1
(L-A105)	HAR	4885†	6.95†	142†	2
2	DTM	4120	6.50	158	1
3	DTM	4120	6.63	161	14a
Ranges		25%	13.5%	16%	
Silver Leaf Mine, along Winnipeg River, S.E. Manitoba, Canada					
1 (L-A109)	MIT	5580	191	3250	3
(L-A109)	DTM	6240	236	3800	1
2	DTM	7150	272	3800	14a
Ranges		20%	35%	14.5%	
Harding Mine, Dixon, New Mexico					
1	MIT	1565	28.4	1815	3
2	DTM	2170	40.2	1850	16
3	DTM	1780	31.5	1770	17
Ranges		32%	35%	4.4%	
Brown Derby Mine, Colorado					
1 (H-503)	MIT	5455	103	1890	14b
2 (H-499)	MIT	5410	104	1920	14b
3	DTM	5550	110	1980	18
4	DTM	6130	118	1925	18
5	DTM	5770	114	1975	18
6	DTM	6870	134	1950	18
7	DTM	5890	130	2170	18
Ranges		25%	36%	14%	

\* MIT, Massachusetts Institute of Technology; DTM, Department of Terrestrial Magnetism, Carnegie Institution of Washington; INS, Institute of Nuclear Studies, University of Chicago; HAR, United Kingdom Atomic Energy Establishment; McM, McMaster University.

† Average of two determinations.

‡ Average of three determinations.

§ McMaster rubidium analysis contaminated; excluded from average.



*Identical Samples (Intercomparison Suite)*

*Sample L-N-45.* Only one sample (from Bikita, Southern Rhodesia) thus far has been analyzed by MSID by four analyst groups (the analyses are given in TABLE 1). No compositional differences between subsamples are apparent in the rubidium and strontium concentration data reported by the several investigators for this sample, which was ground by Backus to a rather fine grain size (0.25 mm.). Three of the reporting laboratories gave standard deviations for their measurements. In TABLE 3A these are compared against the actual ranges of the four pairs of measurements (the Harwell values, for which errors were not stated, fall within the ranges established by the other analyses). It is apparent from the good agreement of the four analyses of this sample that the accuracy limits stated by the several analysts are truly indicative of the absolute accuracies of their isotope-dilution determinations. Hence, at least for old rubidium-rich lepidolites such as Bikita, rubidium and strontium can each be determined routinely to about  $\pm 2$  per cent S.D.; hence Rb/Sr ratios, from which ages are derived, can be determined to  $\pm 2$  per cent or  $\pm 4$  per cent (the improvement resulting from the fact that some errors that enter the concentration determinations cancel out in the ratio).

*Other Intercalibration Suite Samples*

The ages (that is, essentially, the Rb/Sr ratios) reported for the other four intercomparison suite samples in TABLE 1 are also in close agreement. Indeed the entire group of 31 isotope-dilution-age determinations (in which seven localities are represented) reported in TABLES 1 and 2, only three age-ratio measurements differ from the error-weighted averages of all the measurements made on samples from the same locality by more than the standard deviations reported for them. In contrast to the Rb/Sr age ratios, the rubidium and strontium concentration values reported have relatively large ranges. Only the Carnegie Institution and the Massachusetts Institute of Technology groups analyzed all five samples, so the number of cases is not large enough for certainty when stated errors are taken into consideration, but there is in these data at least a suggestion that the several groups of analysts will obtain, in general, slightly different concentration figures for analyses of absolutely identical specimens.

Since, unfortunately, the Massachusetts Institute of Technology analyses had to be made on the residual bulk sample powders rather than on the material sent to the other laboratories and this material in some cases (notably Pala, L-A107) apparently contained considerably more impurities, this deduction must rest primarily upon the  $\text{Sr}^{87}/\text{Rb}^{87}$  ratio data reported by the several analysts. In TABLE 3B the Massachusetts Institute of Technology and Harwell ratios have been recalculated as analysis ratios, using the Carnegie Institution analyses of the various samples as bases. It will be noted in this exhibit that all the Sr/Rb ratios reported by the Massachusetts Institute of Technology and Harwell workers (except two samples with high errors reported) are smaller than the comparable Carnegie Institution analyses. This generalization, it will be seen, holds not only for the intercalibration suite

samples but also for ratios determined on independently collected samples from the Harding and Brown Derby localities. On the average, the Carnegie Institution ratios are about 2 per cent higher than the Massachusetts Institute of Technology values, and a few per cent more than Harwell's values. Scrutiny of the concentration data for L-N45 and L-A107, analyzed by all three groups, indicates that the differences are probably due chiefly to differences in

TABLE 3A  
COMPARISON OF ERROR ESTIMATES AND ACTUAL RANGES OF VALUES FOR  
ANALYSES OF THE LEPIDOLITE FROM BIKITA QUARRY (L-N45).

Quantity measured	Relative standard deviation			Actual range of values
	MIT*	DTM*	INS*	
Rb <sup>87</sup> concentration	±1.6%	±1.2%	±2.8%	4.7%
Sr <sup>87</sup> concentration	±2.1%	±1.4%	±2.9%	7.9%
Relative age	±3.3%	±2.5%	±5.5%	8.5%

TABLE 3B  
EVIDENCE FROM REPORTED Sr<sup>87</sup>/Rb<sup>87</sup> RATIOS ON DIFFERENCES BETWEEN  
LABORATORIES IN STANDARD SOLUTION CALIBRATIONS

Sample	DTM*	MIT*	HAR*	MIT/DTM*	HAR/DTM*
L-N45 Bikita	3800	3590	3650	0.95	0.96
L-A106 Ingersoll	2390†	2290	—	0.96	—
L-A107 Pala	148	(167)††	142	—	0.96
L-A109 Manitoba	3800	(3250)††	—	(0.84)	—
† Harding	1810††	1815	—	1.00	—
† Brown Derby	1970§	1910††	—	0.97	—

\* MIT, Massachusetts Institute of Technology; DTM, Department of Terrestrial Magnetism, Carnegie Institution of Washington; INS, Institute of Nuclear Studies, University of Chicago; HAR, United Kingdom Atomic Energy Establishment; MIT/DTM, ratio of MIT ratio to DTM ratio; HAR/DTM, ratio of HAR ratio to DTM ratio.

\*\* All Harwell values also fall within these ranges.

† Weighted average of three separate analyses.

†† High error quoted for this measurement.

‡ Not part of intercomparison suite.

†† Weighted average of two separate analyses; see TABLE 2.

§ Weighted average of five separate analyses.

strontium standard concentration calibration as the Carnegie Institution and Harwell rubidium data agree quite closely. All the Massachusetts Institute of Technology concentration analyses are lower than both the Carnegie Institution and Harwell comparable analyses. This may be due in part to differences in standard calibrations but, as it is also probably attributable in part to differences in impurity concentration, the calibration difference cannot be determined except via the ratio comparisons, which again indicate that, for samples of equal rubidium concentration, the Carnegie Institution will find about 2 per cent more strontium than either the Massachusetts Institute of Technology or Harwell.

For Varutrask (L-A110), the concentrations reported differ by 20 per cent while the ages agree within 1 per cent. Here the concentration difference probably results from the fact that the sample was distributed in the form of very coarse, uncrushed lepidolite "books."

Many additional comparison analyses such as the above would be required to establish the extent of the differences in standards calibration between the several laboratories. An answer might best be approached through the use of synthetic standards, possibly in the form of ionic solutions of the elements of interest; it would seem that the United States Bureau of Standards might perform a very useful service through the preparation and distribution of such calibration standards.

*MSID Analyses, at Different Laboratories, of Two or More Samples  
from the Same Locality*

Other independently collected samples from these same five localities and several others have been analyzed by MSID by the several investigators in connection with their individual research programs.

Analytically an "age" is of course nothing more than a ratio of concentrations, that is, of daughter nuclide to parent. For a given locality of a single age, this ratio *ideally* should remain constant from sample to sample, regardless of whether the samples vary in parent element concentration. In fact the age ratios given in TABLES 1 and 2 have ranges, for particular samples, of only a few per cent in spite of concentration variations of as much as 25 per cent. Compositional differences between lepidolite samples apparently do not, *per se*, cause differences in apparent age.

The differences in rubidium and radiogenic strontium concentration reported in part doubtless record real variations in lepidolite composition; however, differences in impurity mineral concentration are also partly responsible, since lepidolite samples, as collected, usually include some minerals of markedly lower rubidium content (such as feldspars and quartz) and lepidolite purification techniques may vary markedly both from laboratory to laboratory and from time to time within a single laboratory.

Only negligible concentrations of nonradiogenic, normal-isotope-composition strontium were found in these lepidolites, proving with certainty that no strontium was added to these crystals after they formed, for its composition could have been in the normal range. As regards loss, strontium in the slight concentration produced by radioactive decay in even the most enriched of these samples is very probably below the amount necessary to cause appreciable distortion of the lepidolite structure. Neither is the recoil of the decaying Rb atom sufficiently energetic to cause appreciable structural damage. It further appears, from the good agreement shown by ages for "weathered" and "fresh" samples (in other studies), that the Rb/Sr ratio in a lepidolite is relatively unaffected by weathering processes.

ANALYSES OF THE SAME SAMPLES BY OTHER TECHNIQUES

It is of interest to compare the isotope-dilution analyses just discussed with analyses of the same samples by other techniques. TABLE 4 gives such

TABLE 4  
COMPARISON OF  $\text{Sr}^{87}/\text{Rb}^{87}$  RATIOS DETERMINED BY STABLE ISOTOPE DILUTION,  
OPTICAL SPECTROGRAPHY, AND X-RAY FLUORESCENCE

Locality	MSID ( $\times 10^3$ )*	OS ( $\times 0.127 \times 10^4$ )**	XRF ( $\times 10^4$ )†	
			Proportional counter detector	Scintillation detector
Bikita, Southern Rhodesia	N 45: M-359, D-380 C-391, H-371, 363 other: D-377 av. 373	(AM 365, § 500, 348, 408)	H-366 $\pm$ 7.3	266 $\pm$ 5.0
Bob Ingersoll Mine, S.D.	A 106: M-229, D-232 236, 248 other: D-217, 215, 234, Mc-164†† 230 av. 230	165, 140, 266	H-225 $\pm$ 14	230 $\pm$ 9
Pala, Calif.	A 107: M-17 $\pm$ 2; D-14.8; H-13.9, 14.6 other: D-15.8, 16.1 av. 15.3	19, 29, 18	H-33 $\pm$ 10	20 $\pm$ 10
Winnipeg River, Canada	A 109: M-325; D-380; other: D-380 av. (weighted) 374	374, ‡ 418, 394	H-330 $\pm$ 15	322 $\pm$ 7
Varutrask Harding, Dixon, N.M.	A 110: M-249; D-251, 251 M-182, D-185, 177 av. 181	140	H-252 $\pm$ 11	243 $\pm$ 8
Brown Derby, Colo.	M-189, 192; D-198, 193, 198, 195, 217 av. 197	165, 140	D-190, 195, 192, 198, 197	191, 184
		158		

\* MSID values are ratios of separately determined rubidium and strontium concentrations: M, Massachusetts Institute of Technology; D, Department of Terrestrial Magnetism, Carnegie Institution of Washington; H, United Kingdom Atomic Energy Research Establishment; C, University of Chicago; Mc, McMaster University analysis.

\*\* OS data are average line intensity ratios: All analyses are from Ahrens<sup>5</sup> except "AM," which is from Ahrens and MacGregor.<sup>8</sup>

† XRF data are peak count ratios: H, Herzog;<sup>4</sup> D, Deuser and Herzog (in preparation); the scintillation detector analyses are by Berman and Herzog (unpublished observations); the text gives further details.

†† Average excludes MacMaster analysis.

‡ Seven analyses.

§ This southeast Manitoba sample is used as a comparison standard (see text).



a comparison of Rb/Sr ratio determinations made by optical spectrography and X-ray fluorescence with the isotope-dilution ratios. The optical spectrographic analyses are by L. H. Ahrens and his students and the X-ray fluorescence work was done by my students and myself. Neutron activation data (from Harwell), which are presently at hand only for rubidium concentration, and a few optical spectrograph concentration data, again mostly for rubidium, are given in TABLE 5 along with the comparable MSID concentration values.

### *Optical Spectrography*

It was an emission spectrographic investigation by L. H. Ahrens<sup>5</sup> that aroused interest in the Rb-Sr method once again in the postwar period. In this study the lepidolites were converted to fluorides in an effort to diminish the differential volatility effects that had caused difficulties in earlier attempts to perform such ratio analyses on silicate samples. Ahrens assumed for simplicity that differences in Sr/Rb ratio resulted in directly proportional variations in (Sr 4077/Rb 4202) line intensity ratios (that is, he assumed that both "emission factor" *ns* were 1.000 . . .). If this assumption was correct, raw intensity ratios, times an appropriate factor, should have given correct Rb/Sr ratios and hence ages. To find the conversion factor, Ahrens in his first work made up a synthetic mixed fluoride standard to obtain a particular age; later he used an actual lepidolite from southeast Manitoba (from which L-A109 was later prepared). This sample, which had a Sr 4077/Rb 4202 line ratio of 0.295 average, he assumed to have an age of 2200 m.y. The isotope-dilution analyses, however, indicate that the age is more probably  $2650 \pm 100$  m.y. (this discounts heavily the Massachusetts Institute of Technology analysis of 2300 m.y. on the basis of its large stated error), to which corresponds an  $\text{Sr}^{87}/\text{Rb}^{87}$  ratio of  $3740 \times 10^5$ . Thus a Sr 4077/Rb 4202 ratio of about 0.295 corresponds to an  $\text{Sr}^{87}/\text{Rb}^{87}$  ratio of about 0.037; hence the "conversion factor" is about 0.127. This factor  $\times 10^4$  has been applied to the OS ratios in preparing TABLE 4 to make comparison with the MSID and XRF ratios easier. For the Bikita samples, however, Ahrens and MacGregor<sup>8</sup> had reported only ages; these were based on the southeast Manitoba sample, which was assumed to be  $2200 \times 10^6$  years old. Thus the ratios given for Bikita in TABLE 4 are derived values based on southeast Manitoba = 2650 m.y. and using the conversion factor given above.

Ahrens originally claimed only  $\pm 10$  per cent to  $\pm 20$  per cent precision for his line-intensity ratio ages, and in fact the recomputed OS values given in TABLE 4, while good enough for reconnaissance purposes, especially in 1949, are not comparable in quality to the MSID analyses or even to the XRF data.

While most of the OS analyses are element ratios and thus not directly amenable to comparison with MSID rubidium and strontium concentrations, there is one OS analysis for Sr concentration for comparison (TABLE 5), for the Manitoba sample. This is in acceptable agreement with isotope-dilution analyses made on material from the same locality (considering that there is no reason to expect perfect agreement except in age since the samples analyzed were possibly not identical). There are OS rubidium analyses for samples from three of these localities. They run 10 per cent to 20 per cent higher than the (pos-

TABLE 5

COMPARISON OF  $\text{Sr}^{87}$  AND  $\text{Rb}^{87}$  CONCENTRATION ANALYSES BY NEUTRON ACTIVATION AND OPTICAL SPECTROGRAPH WITH ISOTOPE-DILUTION RESULTS\*

	$\text{Rb}^{87}$ (ppm)			$\text{Sr}^{87}$ (ppm)		
	Isotope dilution (range)	Optical spectrograph	Neutron activation	Isotope dilution	Optical spectrograph	Neutron activation
Bikita						
L-N45 raw	9170 <sup>3</sup>					
L-N45 i.s.	8930-9400		9660, 9620 <sup>2</sup>			
Other	8750					
Black Hills, S.D.						
L-A106r	3505 <sup>3</sup>	3430 <sup>6,7</sup> (4360) <sup>6,7</sup> §				
L-A106 i.s.	3280-3500					
Other	3140-3370	3700 <sup>26</sup>				
Pala, Calif.						
L-A105r	3870 <sup>3</sup>		4930, 5000 <sup>2</sup>			
L-A105 i.c.	4810-4980					
Other	4120	5700 <sup>26</sup>				
Southeast Manitoba, Canada						
L-A109r	5880 <sup>3</sup>	5880 <sup>6,7</sup> (7480) <sup>6,7</sup> §		191 ± 18 <sup>3</sup>	205 ± 12 <sup>6,7</sup>	
L-A109 i.c.	6240			236 ± 5 <sup>1</sup>		
Other	7150	(7420) <sup>6,7</sup> § 7100 <sup>27</sup>				
Varutrask						
L-A110r	5140 <sup>3</sup>	4770 <sup>6,7</sup> (6060) <sup>6,7</sup> §				
L-A110 i.c.	5810, 5810					
G-1 (Standard granite)	218, 215 <sup>19</sup>	Total Rb (ppm) 590 <sup>20</sup> 221, 550 <sup>20</sup> 254, 250 <sup>21</sup> 253 <sup>9</sup>		230, 233, 236 <sup>19</sup>	900 <sup>20</sup> 120 <sup>20</sup> 250 <sup>20</sup> 280 <sup>21</sup>	252 <sup>28</sup>
W-1 (Standard diabase)	27.9, 29.1 <sup>19</sup>	15 <sup>23</sup> 27, 64 <sup>20</sup> 29, 20 <sup>21</sup> 26 <sup>9</sup>		182, 172 <sup>19</sup>	220 <sup>21</sup> 420 <sup>20</sup> 120 <sup>20</sup> 250 <sup>20</sup>	172 <sup>28</sup>
Forest City Chondrite	3.5 <sup>23</sup>	6 <sup>23</sup> 3.01, 3.06 <sup>2</sup> (3) <sup>9, 22</sup> §		9.8 <sup>23</sup>	180 <sup>21</sup> 180 <sup>21</sup> 10 <sup>24</sup>	
	2.97, 2.77, 2.85, 3.00	5.8 <sup>10</sup> †		10.5, 9.6, 9.7 11.0		
	Avg. 2.90†			Avg. 10.2 <sup>2</sup>		

\* Lepidolite isotope-dilution references are given in TABLE 1.

† Schumacher (personal communication).

‡ Flame photometer analysis.

§ Values in brackets are given in references; nonbracketed values are "corrected" by dividing by 1.27 on the basis of MSID work (see text).

sibly) comparable isotope-dilution analyses, and the difference is greatest for the sample with the lowest rubidium content. It is in the direction that will make the OS age ratios computed, using these analyses, too small; the ages computed from the data of Ahrens and Gorfinkle<sup>6</sup> (using the present half life) actually are too small.

If we assume that these OS analyses and the Massachusetts Institute of Technology MSID analyses were made on the same materials (if they were not, the MSID material should have been more pure and hence slightly higher in rubidium) and that the Massachusetts Institute of Technology Manitoba result is correct, the OS measurement is too high by about 27 per cent. Correcting the OS analyses for the Bob Ingersoll Mine and Varutrask by this amount in fact makes them agree quite reasonably with the MSID analyses.

The optical-spectrograph concentration analyses for rubidium and strontium were made by the internal standardization technique. For strontium the standard was barium, while for rubidium potassium was used as a standard.<sup>6</sup> It was added in the form of albite. The other results were based on an "addition method" analysis of the southeast Manitoba sample in which the rubidium was added as chloride; it was recognized that sensitivity for chloride and silicate rubidium might be different but no correction was attempted. Also, the use of potassium was recognized to be risky, because it is present in lepidolites in substantial concentrations.

I feel that it is entirely possible that an optical spectrographic Rb-Sr method of age determination of acceptable accuracy might still be developed, for lepidolites and other minerals containing negligible strontium at crystallization, through the use of standard samples analyzed by isotope dilution and/or neutron activation.

### *X-Ray Fluorescence Analyses*

The X-ray fluorescence results, which are also in the form of element ratios only at this time, will be seen to be surprisingly accurate when compared against the isotope-dilution results taken as "standards."

I do not propose to discuss the techniques used in this X-ray fluorescence work in any detail here; our group has done this in a series of papers in press and in preparation. For present purposes it is sufficient to say that as time has gone by techniques have been changed (and are still being modified). A major change has been the replacement of the gas-flow proportional counter detector used by myself<sup>4</sup> (results marked "H") and Werner Deuser (unpublished results marked "D"), by a scintillation detector now being used by Roslyn Berman (unpublished results marked "B").

The amount of strontium in these lepidolites, excepting only samples such as Bikita, which are both very old and very high in rubidium, is so small (100 ppm) that high precision is achievable only by replicate runs and by an extensive use of peak overlap, background shape, and other correction factors, at least with our present techniques. However, certainly even in its present form the method offers great promise for the determination of rubidium; it appears that it can be made at least as accurate as isotope dilution and neutron activation for samples having more than about 500 ppm rubidium. Lepidolites have approximately 20 times this concentration.

Thus far we have used XRF principally for reconnaissance and as a check on our isotope dilution work in order to find gross errors. However the technique has proved to be even better than this; as the data for ancient, high-rubidium lepidolites show, it is possible even now to obtain results comparable in accuracy to these obtained by isotope dilution and to get them in about one tenth the time once the technique is established (even setting up the technique takes far less time than it does for MSID). In addition, X-ray fluorescence of course has the unique advantage of being a nondestructive technique, so that completely identical samples can be rerun as many times as seems advisable in any number of different laboratories.

### *Neutron Activation Analyses*

Only two of these lepidolite samples have until now been analyzed by neutron activation and these for rubidium only. These analyses, made at Harwell by Webster *et al.*,<sup>2</sup> are in quite good agreement with the stable isotope-dilution analyses. However, they in fact agree better with the Harwell MSID analyses<sup>2</sup> than with those made elsewhere; this apparently again indicates that small differences in standard calibration exist among the several laboratories.

### *Comparison of Methods*

Neutron-activation analyses have in fact been made on some nonlepidolite materials that have been analyzed by the other techniques, and these results provide valuable additional data on the merits of the several techniques. In TABLE 5 I present all the rubidium and strontium data for the powdered rock standards G-1 (a granite), W-1 (a diabase), and the chondritic meteorite Forest City, different fragments of which were analyzed by the several investigators. The activation work is by Smales and Cabell<sup>9</sup> and by Webster *et al.*<sup>2,28</sup> One flame photometer result (by Edwards and Urey<sup>10</sup>) is also included.

The optical spectrographic results are those reported by Fairbairn *et al.*<sup>20</sup> and Ahrens<sup>21</sup> (pages 23, 25, 28, 29). For this technique analyses made at five laboratories show wide ranges.

When the concentration level of about 1 ppm for these elements is reached, the fact that activation analysis is inherently free of contamination problems begins to manifest itself. Certainly neutron activation is the more foolproof technique from this standpoint, as recent neutron activation checks on previous isotope dilution rubidium and uranium analyses indicate very convincingly.

### CONCLUSIONS

A comparison of Rb-Sr analyses of five lepidolite samples, comprising an intercomparison suite and ranging in age from  $100 \times 10^6$  to  $2600 \times 10^6$  years made in four laboratories, indicates that reproducibilities of better than  $\pm 4$  per cent can be obtained routinely for the ratio of daughter  $\text{Sr}^{87}$  to parent  $\text{Rb}^{87}$  and thus, for apparent age, by the mass-spectrometric stable-isotope-dilution technique. Concentrations of rubidium and strontium can probably be determined today with precisions of better than  $\pm 2$  per cent by this method. Interlaboratory agreement is nearly as good as intralaboratory precision for Rb/Sr age ratios, indicating that the concentrations, and especially ratios, found by



isotope-dilution analysis are highly accurate in an absolute sense as well as reproducible within a particular laboratory. However, accuracy could apparently be improved still further by the exchange of primary standards among laboratories for comparison of analyses and intercalibration.

For the intercomparison suite of lepidolites, the neutron-activation rubidium analyses are in good ( $\pm 3$  per cent) agreement with the isotope dilution results, and the X-ray fluorescence Sr/Rb count ratio determinations (which required somewhat less labor than either the isotope-dilution or neutron-activation results) are apparently comparable in accuracy, for ancient samples, with the results obtained by the more expensive techniques. The early optical spectrographic analyses of samples from some of these localities (which required an intermediate amount of labor) were apparently reasonably accurate for strontium but erratic and generally high for rubidium and hence for Rb/Sr ratio and age. It is believed, however, that this technique could be greatly improved by the use of standards whose rubidium and strontium concentrations were determined by neutron activation or isotope dilution.

A comparison of isotope-dilution-age determinations of independently collected lepidolites from particular sites indicates that rubidium in lepidolite may vary by as much as 30 per cent but that no differences in apparent age arise from this cause. Hence, there probably has been no appreciable leaching of parent Rb<sup>87</sup> or daughter Sr<sup>87</sup> from these samples. If strontium loss has occurred, it must have been essentially proportional to rubidium concentration and, since this seems improbable, such loss seems equally unlikely. The very low ( $< 1$  ppm) nonradiogenic strontium content of these lepidolites indicates low original strontium content and no addition of strontium during sample history.

Readers have no doubt observed that there are many "missing links" in the data just presented. Quite obviously there is a continuing need for intercomparison studies of the type described here to establish the degree of reproducibility between laboratories of dilution analysis. There is even greater need, however, for analyses of carefully selected "standard" samples by more than one technique. Such studies will provide an indispensable aid to the improvement of analytical accuracy in all techniques.

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# THE POTASSIUM-ARGON METHOD: THE PROBLEM OF POTASSIUM ANALYSIS

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I have always thought that it is one of the great curiosities of modern analytical chemistry that it is possible to analyze for argon, which occurs to the extent of about 0.01 to 0.001 cc. of gas per gram in a sample, to a much greater accuracy and with more confidence than it is possible to analyze for one of the major elements, namely potassium. This statement may appear surprising to

TABLE 1  
ANALYSES OF B-3203 FOR POTASSIUM

Potassium (%)	Method	Analyst
7.80 $\pm$ 0.07	Neutron activation	J. Winchester, M.I.T.*
7.40	Flame photometry, Li, internal standard	H. Faul, United States Geological Survey, Washington, D.C.
7.42	Laurence-Smith: $K_2PtCl_6$	S. Goldich, University of Minnesota, Minneapolis, Minn.
7.79	Flame photometry, direct	L. Kovich, University of California at Berkeley, Berkeley, Calif.
7.58 $\pm$ 0.03	Flame photometry, Li internal standard	W. Pinson, M.I.T.
7.40 $\pm$ 0.06	Gravimetric; $KClO_4$	W. Pinson, M.I.T.
7.71 $\pm$ 0.07	Flame photometry: Li internal standard	R. W. Stoenner, Brookhaven National Laboratory, Upton, N.Y.
7.68 $\pm$ 0.06	Laurence-Smith: $K_2PtCl_6$	R. W. Stoenner, Brookhaven National Laboratory, Upton, N.Y.
7.76	Flame photometry, Li internal standard	George Edwards, Shell Development Co.
7.59, 7.60	Isotope dilution	L. E. Long, Lamont Geochemical Laboratory, Palisades, N.Y.
7.56	DU flame photometry	Sydney Abbey, Canadian Geological Survey, University of Ontario, Ottawa, Canada

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some; nevertheless this has been the experience of my associates and myself. Several years ago H. W. Fairbairn prepared a sample biotite, B-3203, as an interlaboratory standard. It was distributed to a number of different laboratories. Considerable care was taken to insure homogeneity in this sample. This biotite standard was meant to serve as a potassium, rubidium, strontium, and argon standard for those engaged in age-measurements work. A number of workers have forwarded their results on their potassium analyses to us and report on this now. We have to date received but one rubidium analysis on this sample.

In discussions of the relative abundances and decay constants of potassium and rubidium and in age studies in which rubidium-strontium and potassium-argon age measurements are compared, it is imperative to have confidence in analyses for potassium and rubidium. I think it is well for us to continue to put our minds and energies to work on interlaboratory standards such as

B-3203. The results of the potassium analyses on this standard from a number of different laboratories, shown in TABLE 1, range from about 7.4 to 7.8 per cent potassium. This is a range of about 6 per cent, which is about the range of uncertainty of the values of the decay constants of these elements, I believe. With regard to potassium analyses by stable-isotope dilution analysis, we feel that we can get the same precision and accuracy by flame photometry.<sup>2</sup> There is, of course, less work and expense involved, and the solid-source mass spectrometer is left free for rubidium-strontium analyses. We do, however, frequently confirm our flame photometer results by both mass spectrometry and gravimetric analysis.

Neutron activation analysis by J. W. Winchester at Massachusetts Institute of Technology gives the highest potassium value for B-3203.<sup>1</sup> Our gravimetric analysis agrees quite well with the gravimetric analysis by S. S. Goldich of the United States Geological Survey, Washington, D.C., and is lower than the flame photometer results, which are in general agreement. I have the greatest confidence in the gravimetric method. However, it is probably the safest course to assume that an average value of all the results in TABLE 1, namely about 7.61 per cent, is nearest to the truth.

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#### Discussion of the Paper

G. J. WASSERBURG (*California Institute of Technology, Pasadena, Calif.*): I have some comments to make concerning potassium analyses. Some time ago, J. W. Winchester at the Massachusetts Institute of Technology suggested that there was a loss of potassium by volatilization during the dissolution procedure. My associates and I have attempted to check this effect using somewhat different techniques and have not found any evidence in support of this idea. Synthetic samples of silicates and KCl were dissolved with HF and H<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The time of evaporation was also varied. The recovery was 100 per cent.

Similarly a mica and a known mixture of mica and KCl were processed and analyzed. The measured potassium content agreed with the value calculated for the mixture. These experiments were carried out on biotites, muscovites, and phlogopites. In no case was any effect noted to within 1 per cent of the K content. There is, of course, the possibility that only the K in the silicate is volatilized.

In addition to this matter of volatilization G. W. Wetherill, V. Wen, and I have run a suite of samples that includes biotites and muscovites by both isotope-dilution and flame-photometric procedures. With the exception of one sample, these results are in agreement within 1 per cent. The usual precision of our flame photometric analyses on repeat runs is 1 per cent.

S. S. GOLDICH (*United States Geological Survey, Washington, D.C.*): My



colleagues and I did the original work at the University of Minnesota, Minneapolis, Minn., and since then we have been carrying on a program to check the J. Lawrence Smith method. It is an extraction method that, in the hands of a good chemist, gives good reproducible results, but it is hard to detect a bias in a method that might give low results.

I do not have the final results, but we have taken great pains to try to minimize losses due to volatilization. We are quite willing to say that the result is somewhat low, perhaps 1 or 2 per cent. The probable answer lies between 7.5 and 7.6 per cent. This would make our original determination no more than a few per cent low.

L. LONG (*Lamont Geological Observatory, Columbia University, Palisades, N.Y.*): Two results were obtained at Lamont on the Massachusetts Institute of Technology standard by the isotope-dilution method: We got 7.59 and 7.60. Also, we tried one experiment similar to Wasserburg's. Once we were careful not to bake our samples, and another time we heated them overnight on a hot plate at a very high temperature and obtained identical results.

PINSON. Thank you for the new result. This isotope-dilution result appears to agree with the average of the flame-photometric results, using lithium as an internal standard.

To add a word concerning the possibility of potassium loss by volatilization during analysis: Winchester thought at first that he had detected some loss but, while repeating his experiment, he found the apparent loss of potassium was due to an inaccurate counting technique. I have carried out any number of such experiments and have been unable to detect any such volatilization. I hope that this is true, because it certainly would be disquieting to learn that we had been evaporating off potassium all these years without knowing it.

R. K. WANLESS (*Geological Survey of Canada, Ottawa, Ont., Canada*): Two determinations have been made on the Massachusetts Institute of Technology standard biotite B-3203 by Sydney Abbey in our laboratory, using a DU flame photometer and handled in a routine manner with the rest of the potassium determination. The values are 7.43 and 7.49. On a new portion of B-3203 recently received from the Massachusetts Institute of Technology, values of 7.57 and 7.63 were obtained (Abbey and Maxwell, 1960).

R. E. FOLINSBEE (*University of Alberta, Edmonton, Alta., Canada*): My associates and I made a considerable number of runs with a Perkin-Elmer flame photometer on NBS-70, a feldspar containing 12.58 per cent  $K_2O$  according to the United States Bureau of Standards. Consistently we obtained results that were 1 per cent high on five runs, which agreed within one tenth of 1 per cent at 12.68. We have made five subsequent runs with J. Lawrence Smith fusion, followed by tetraphenyl-boron precipitation, and these result in 12.58 within about 0.03 per cent  $K_2O$ , so that we agree with Goldich that the J. Lawrence Smith fusion followed by a precipitation method, runs about 1 per cent low as compared with the flame photometer method.

PINSON: That is interesting, but in the gravimetric method I used, I did not employ the J. Lawrence Smith method for extraction. I used only a chemical solution followed by precipitation as potassium perchlorate, and the results agreed with your analyses, gravimetrically.

GOLDICH: There is a real difference here of about 6 per cent from the lowest to the highest result.

PINSON: The highest result was the one reported by neutron activation. Therefore, if this is withdrawn, it reduces things somewhat.

GOLDICH: If it were just a difference between 7.4 and 7.5 per cent, I should not quibble; but the difference between 7.4 and 7.8 per cent is a substantial one: about 6 per cent approximately.

FOLINSBEE: We ran the NBS-70 feldspar, using an internal standard and Perkin-Elmer flame photometer, and arrived at a result 2 per cent too high. We went to the other extreme; we said we were wrong and corrected back by that 2 per cent to gravimetric values.

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# THE BASE-EXCHANGE EFFECTS ON POTASSIUM-ARGON AND RUBIDIUM-STRONTIUM ISOTOPIC AGES

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KULP: My associates and I have begun a study of the base-exchange effects on the K-Ar and Rb-Sr isotopic ratios in an attempt to understand this potential cause of discordancy. Preliminary experiments show that argon is not driven into the structure by recoil and subsequently retained since no excess

TABLE 1  
BASE-EXCHANGE EXPERIMENTS ON METAMORPHIC BIOTITE

Sample	Weight, mesh	Solution	Time (weeks)	Original K (%)	K after leaching (%)	Original $A^{40}/K^{40}$	$Ar^{40}/K^{40}$ after leaching
JE 2-59 age: ~810 m.y.	4 gm. 60-80	1 l. of 1 molar $MgCl_2 \cdot 6H_2O$ $\frac{Mg}{K} \cong 150$	1	7.24	1.64	0.0590	0.0481
JE 2-59 age: ~810 m.y.	40 gm. coarse (60-80)	2 l. of 1 molar $MgCl_2 \cdot 6H_2O$ $\frac{Mg}{K} \cong 30$	4	7.24	6.93	0.0590	0.0526
L-90 PUF25 age: ~1500 m.y.	10.0 gm.	1 l. of 1 molar $MgCl_2 \cdot 6H_2O$ $\frac{Mg}{K} \cong 100$	4	5.69	4.36	0.1380	0.1082

All samples stirred continuously in closed containers; temperature ~100° C.

\* Radiogenic.

argon has been observed when potassium is removed by the base-exchange process. Thus it appears impossible to obtain a K-Ar age in a mica from an igneous or metamorphic rock that is too high. Three leaching experiments have been carried out under the conditions shown in TABLE 1. In all cases the  $Ar^{40}/K^{40}$  ratio was found to have decreased, indicating that some argon is leached preferentially to potassium. This was the situation even after 80 per cent of the potassium had been removed. Thus we conclude that the argon is not retained into the lattice relative to potassium under base-exchange conditions and that therefore the K-Ar method should always give a minimum age. In leaching experiments of this type it is seen that the ratio  $Mg/K$  and the grain size of the mineral being leached are critical in determining the amount of potassium leached away. Therefore in future experiments the biotite will be ground to a much finer mesh, and the leaching solution will be continuously removed after contacting the biotite in a column.

BASSETT: I have also run some samples similar to these and found that about two thirds of the potassium and about five sixths of the argon were removed, thus lowering the  $\text{Ar}^{40}/\text{K}^{40}$  ratio to about one half what it was originally. I also ran a naturally altered biotite that had been altered to chlorite and found that this showed very similar results: about one third the potassium and about two thirds of the argon were removed, thus lowering the  $\text{Ar}^{40}/\text{K}^{40}$  ratio to about one half.



# THE RETENTIVITY OF RADIOGENIC ARGON IN GROUND MICAS

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As is known, filing and grinding of minerals often result in damage to their crystal structure. Thus, for example, C. MacKenzie<sup>1</sup> in studying the grinding effect on muscovite found that the powder diagram of the ground mineral differs from the X-ray photograph of the less damaged filed mica, not only in having less intense lines but also in possessing distinct new lines. The breakdown of the crystal structure of the muscovite in case of dry grinding in the agate mortar was also observed from the thermograms, cation-exchange capacity, and the dehydration curves.

Micas, and the muscovite among them, are the most suitable materials for K-Ar dating. The main parameter that determines the retentivity of radiogenic argon in micas is the activation energy.

The changes of the crystal lattice of micas caused by grinding could be expected to affect the value of the activation energy and, consequently, the diffusion rate of the radiogenic argon. In addition some losses could occur even during vigorous grinding. To investigate the effect of grinding on the retentivity of radiogenic argon in micas we took samples of micas mechanically ground, filed, and cut. Fine fractions were sieved through a 200-mesh sieve. X-ray photographs of the fine samples were made, and corresponding values of activation energy of the argon isolation were obtained.

Muscovite was studied most thoroughly. X-ray analysis was made by the powder method, using Cu-K radiation. The camera diameter was 66 mm., the sample diameter was 0.7 mm., and the intensity of the lines was determined visually.

The correction of  $d$  value was made by a special X-ray photograph of NaCl that enabled us to calculate the errors to the tenth of one per cent for values less than  $3kX$ .

As a result of these powder diagrams we found that the filed micas differ from the micas ground mechanically. This difference is clearly seen after the first comparison of photos and has its base in the fact that filed micas have powder diagrams with a larger number of considerably sharper lines than powder diagrams of micas ground mechanically.

Our powder diagram calculations have shown that the inner reconstruction of the mica structure affected by short period but energetic grinding is rather great.

This phenomenon is clearly seen on our sample of phlogopite.

From comparing intensities and  $d$  values of phlogopite (TABLE 1) ground by different methods, not only the change but also the loss of a number of lines on X-ray photographs may be seen. It should be noted that, unlike the

muscovite, lines on the X-ray photographs disappear here as well as in the area of "big angles."

It should be mentioned that two new lines not to be found on the photograph of the filed phlogopite appear on the powder diagram of the phlogopite ground mechanically, testifying to a considerable reconstruction and to a possible formation of a new structure.

Regarding the difference in the powder diagrams of our muscovite sample

TABLE 1

No.	Muscovite*				Phlogopite**			
	Filed		Ground mechanically		Filed		Ground mechanically	
	I	d	I	d	I	d	I	d
1	3	3.90	3	3.98	2	4.08	5	3.84
2	5	3.55	5	3.62	10	3.35	10	3.34
3	9	3.35	9	3.48	3	3.25	1	3.17
4	4	3.20	3	3.19	8	2.508	3	2.926
5	5	3.10	5	3.10	9	2.164	2	2.720
6	7†	2.862	6†	2.857	10	2.002	5	2.640
7	5†	2.789	3†	2.790	5	1.900	4	2.511
8	10	2.586	10	2.591	6	1.847	5	2.438
9	2	2.471			3	1.746	3	2.274
10	7	2.375	6	2.370	10	1.661	5	2.187
11	2	2.255			1	1.588	8	2.020
12	6	2.189	4†	2.191	9	1.537	10	1.548
13	8	2.130	7	2.134	2	1.479	8	1.376
14	3	2.050	3	2.058	2	1.435	3	1.336
15	10	1.988	10†	2.009	1	1.406		
16	2	1.952			10	1.362		
17	2†	1.868			3†	1.312		
18	1	1.726			3	1.255		
19	8	1.645	6†	1.65	3	1.221		
20	5	1.590	5	1.59	4	1.128		
21	5†	1.555	5	1.56	2†	1.083		
22	4†	1.521	3	1.53	6	1.060		
23	10	1.494	8	1.50	5	1.046		
24	2	1.450			2	1.017		
25	3	1.430			7†	0.9948		
26	1	1.409			7†	0.9690		
27	8	1.350			6	0.9064		
28	5	1.335	4	1.36	3†	0.8825		
29	1	1.317	2	1.32	3	0.8665		
30	8	1.297	5	1.30	7	0.8492		
31	4†	1.264	2	1.27	6	0.8359		
32	8	1.246	3	1.25	6	0.8176		
33	4†	1.220						
34	2	1.205						
35	2	1.193						
36	3†	1.164						
37	2	1.130						
38	5	1.112						
39	2	1.100						

\* Unit cell dimensions:  $a = 5.20$ ,  $b = 8.98$ ,  $c = 20.05$ .

\*\* Unit cell dimensions:  $a = 5.21$ ,  $b = 9.19$ ,  $c = 21.70$ .

† Diffused lines.

‡ All other lines are sharply diffused.

prepared by different methods, it is not very large. This difference is mainly characterized by the disappearance of lines beginning with 1.220 Å, by the partial disappearance of some lines of smaller intensity with large  $d$  values, and by the increase of the unit-cell parameter of the mineral.

Therefore mechanical grinding of micas results in damage to their structure.

The method of determining activation energy based on the Grinberg theory<sup>2</sup> regarding the general regularities of degassing in heated metals has already been described in previous papers.<sup>3,4</sup> It should be once again mentioned that, in an estimation of the activation energy, the dependence of loss of radiogenic argon on time at different temperatures must be studied. To investigate the kinetics of  $\text{Ar}^{40}$  loss, we used the mass spectrometer with a molecular leak into the ionization chamber.

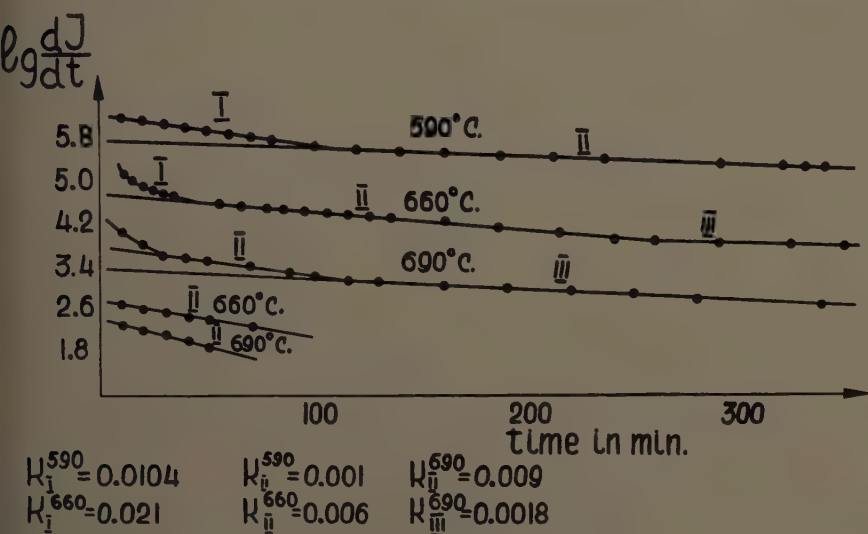


FIGURE 1.

The gases in the mixture go to the mass spectrometer independent of each other and, consequently, the intensity of the peak  $\text{Ar}^{40}$  in question changes proportionally to the change of its partial pressure.

The gas isolated from the mineral was continuously pumped out by the vacuum pump. During the measurements, the vacuum pump tap was closed and the peak intensity during time-unit was measured. To pass to the absolute amounts of the argon loss, the calibration on the known pressure  $\text{Ar}^{40}$  in inlet vacuum system was made.

Some experimental curves obtained from the ground mica are given in FIGURE 1. Similar curves are obtained for the filed mica.

From these figures, where the rate of argon isolation is plotted on the abscissa, it may be concluded that in all cases there are curves consisting of separate rectilinear sections.

This testifies to the fact that argon in the mineral is in several positions,

each being characterized by a definite heat of diffusion. Considering processes of argon loss from different positions independent of each other, we can find the straight lines belonging to any of its positions in the mineral by means of corresponding amendments (TABLE 2).

TABLE 2  
THE "PERTI-VARAKA" MUSCOVITE

Name of fraction	Total content	Amount of Ar <sup>40</sup> connected with E = 93,000	Amount of Ar <sup>40</sup> connected E = 18,000	Amount of Ar <sup>40</sup> connected with E = 37,000
Cut mica	10.03 · 10 <sup>-4</sup>	6.42 · 10 <sup>-4</sup>		
Filed mica	9.74 · 10 <sup>-4</sup>		2.04 · 10 <sup>-4</sup>	5.76 · 10 <sup>-4</sup>
Ground mica	7.06 · 10 <sup>-4</sup>		2.47 · 10 <sup>-4</sup>	2.47 · 10 <sup>-4</sup>

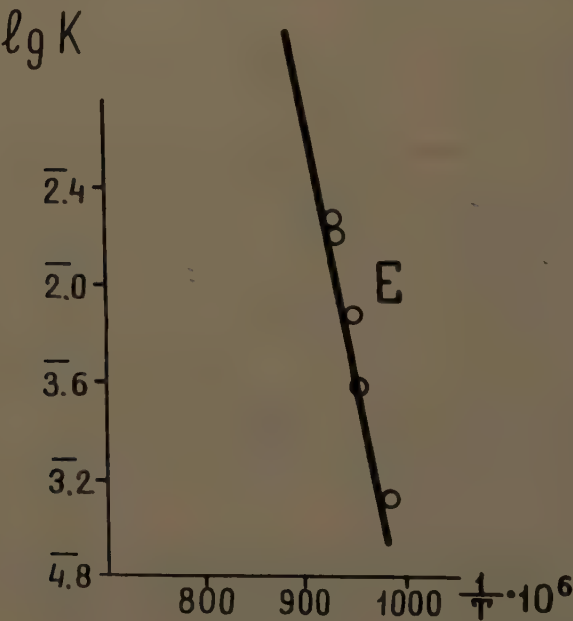


FIGURE 2. E = 93,000 cal./gm. atom of argon.

The slopes of the straight lines being determined, the general amount of Ar<sup>40</sup> in separate positions can be found by means of integration, taking into account the calibration data.

Later, in estimating the values of activation energy, we plot  $\ln k$  on the ordinate axis and  $(1/T) \times 10^6$  on the abscissa. The activation energy (FIGURES 2 through 5) is estimated from the slope of the resulting straight line.

The unknown value of the activation energy for the cut muscovite amounts to 93,000 cal./gm. atom Ar, which agrees with our previous estimates.<sup>3</sup> According to the estimates  $6.42 \times 10^{-4}$  cm.<sup>3</sup> Ar<sup>40</sup>/gm. is connected with this value,



which makes 64 per cent of the total content,  $10.03 \times 10^{-4} \text{ cm}^3 \text{ Ar}^{40}/\text{gm}$ . The rest of the argon is connected with larger values of the activation energy.

For the other two mica fractions in the temperature interval from  $500^\circ \text{ C}$ .

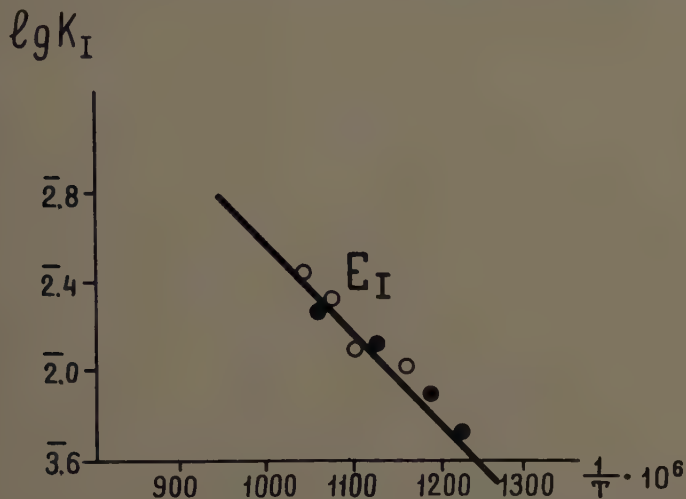


FIGURE 3.  $E = 18,000 \text{ cal./gm. atom of argon}$ ;  $\bullet$  = filed micas;  $\circ$  = ground micas.

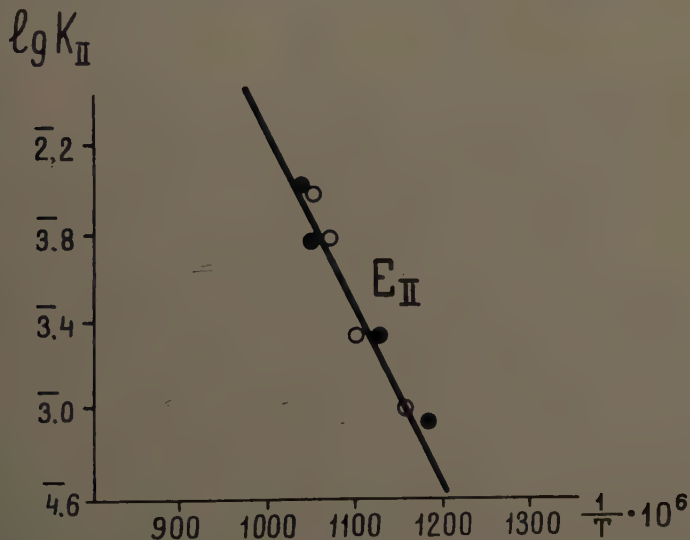


FIGURE 4.  $E = 37,000 \text{ cal./gm. atom of argon}$ ;  $\bullet$  = filed micas;  $\circ$  = ground micas.

to  $800^\circ \text{ C}$ ., 3 values of activation energy were found, equal to 18,000, 37,000, and 72,000 cal./gm. atom Ar, respectively.

Thus a set of values of activation energy connected with much easier isolated argon was found for the fine muscovite fractions. This undoubtedly proves the damaged crystal structure in the ground mica fractions.

In spite of the fact that identical values for the activation energy were obtained for both small mica fractions, the amount of argon connected with them is far from being the same.

Thus, for example, the amount of argon in its first two positions for the filed sample amounts to  $7.8 \times 10^{-4}$  cm.<sup>3</sup> Ar<sup>40</sup>/gm., whereas it comes only to

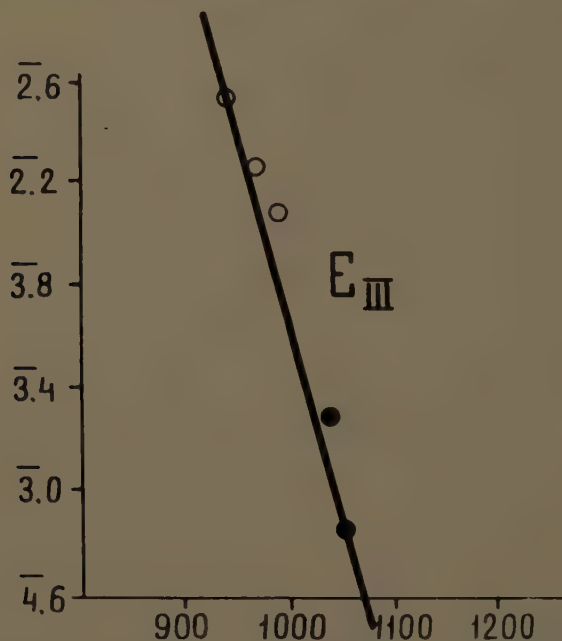


FIGURE 5. Key: ● = filed micas; ○ = ground micas; 72,000 cal./gm. atom of Ar.

TABLE 3

Mineral name	Original content	Content of Ar <sup>40</sup> in cm. <sup>3</sup> gm. in mica after filing	Content of Ar <sup>40</sup> in cm. <sup>3</sup> gm. in the ground mica	Loss (%)
"Perti-Varaka" muscovite	$10.03 \cdot 10^{-4}$	$9.74 \cdot 10^{-4}$	$7.06 \cdot 10^{-4}$	30
"Ruby lode" muscovite	$9.83 \cdot 10^{-4}$	$9.85 \cdot 10^{-4}$	$7.5 \cdot 10^{-4}$	24
"Aldan" phlogopite	$9.57 \cdot 10^{-4}$		$6.66 \cdot 10^{-4}$	30

$4.94 \times 10^{-4}$  cm.<sup>3</sup> Ar<sup>40</sup>/gm. in the sample ground mechanically. In addition it should be mentioned here that a large loss of argon amounting to 30 per cent was found to occur in the mica sample mechanically ground. The same losses were found to occur in other ground micas (TABLE 3).

We may conclude from these data that grinding of micas results in considerable changes of their crystal structure, appreciable changes occurring in the samples ground mechanically.

Considerable decrease of the activation energy for the loss of argon in the

ground micas facilitates its removal. This accounts for the considerable increase of the amount of argon isolated from these fractions already at low temperature (FIGURE 6).

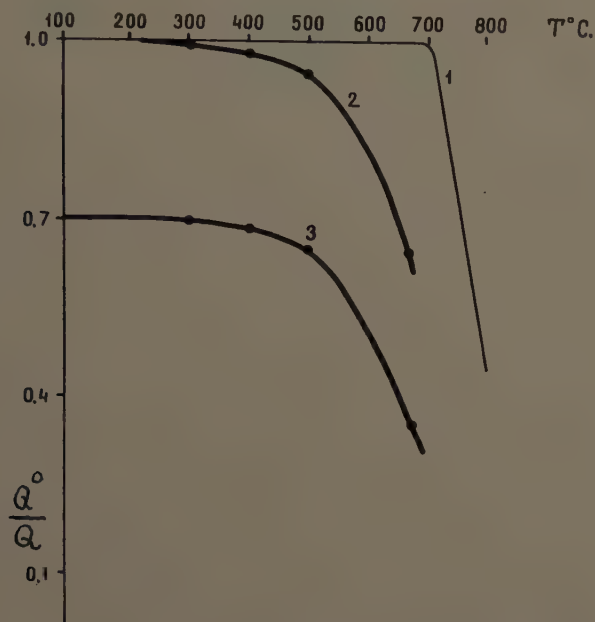


FIGURE 6.  $Q$  = total content of argon;  $Q^\circ$  = amount of argon remaining after heating for two hours; curve 1 = cut micas; curve 2 = filed micas; curve 3 = ground micas.

TABLE 4  
CONTENT OF WATER IN THE "PERTI-VARAKA" MUSCOVITE FOR DIFFERENT FRACTIONS OF GRINDING

Name of fraction	Content (H <sub>2</sub> O) (%)
Cut mica	4.44
Filed mica	5.6
Ground mica	6.06

It should be noted in conclusion that the water content (TABLE 4) was determined in all samples of micas. It follows from the given tables that chemical changes occur as a result of grinding micas.

In summary, we can make the following conclusions:

(1) The X-ray photographs and the determined values of the activation energy for argon loss prove the damage of the crystal structure of micas on grinding. Particularly considerable changes occur in micas ground mechanically.

(2) The micas mechanically ground lose about 30 per cent of the included argon.

(3) To obtain reliable data on Ar/K ratios, scissors should be used to cut the mica.

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# RADIOGENIC ARGON IN MINERALS AND ITS MIGRATION

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## *Introduction*

The considerable number of publications devoted to the K-Ar method of absolute age determination is evidence of increasing interest in this subject. Very often data obtained by the K-Ar method disagree with those of other methods. Obviously most of these disagreements are due to the radiogenic-argon leakage from minerals and rocks during geological time. In order to accept the method, we therefore must first discover the causes and mechanisms of this leakage and how to consider these quantitatively.

The question arises whether the solution of this problem is obtainable by purely geological considerations. Apparently this is not the case because of the potential features of argon leakage from minerals and rocks during geological time, that is, the leakage may or may not manifest itself, depending on unknown conditions. The evaluation of these conditions should be based entirely on a knowledge of the detailed geological history of the specimen studied, which in turn must be expressed in terms of time intervals characteristic for the existence of the specimen. Thus we arrive at a single equation with two unknown quantities, to an *idem per idem* circle of logic.

The solution consists in making use of the possibilities of associated branches of science to convert our single equation into a system of solvable equations in order to investigate geochronologic problems in terms of this resolved system. Modern solid-state physics and physical chemistry are able to give us the desired complementary equations. The geological aspect of the problem characterizes, therefore, changes and argon losses, which might have occurred in some minerals during their existence, while the nature of the argon losses may be cleared only by a study of the physical and chemical aspects of the problem by laboratory means.

In this connection it is difficult to justify the proposal of some authors (Vasserburg *et al.*, 1956; Follinsbee *et al.*, 1956; Shillibeer and Burwash, 1956; Vasserburg *et al.*, 1957; Goldich *et al.*, 1957) to use artificially diminished empirical branching ratios of  $K^{40}$  equal to 0.085:0.09, in order to consider virtual argon losses in feldspars. This is a method perhaps quite practicable in calculating average lifetimes of individual minerals but doubtfully applicable to an exact discipline such as geochronology. Any desired number can be obtained by multiplying any other arbitrary number by a properly chosen constant.

The most recent conclusion of most investigators has been that all of the observed argon losses in minerals are due to its diffusion in the crystal lattice, but the nature of this diffusion is treated differently by different authors. It is incomprehensible that a given mineral in some cases exhibits complete argon preservation, while in other samples of the same mineral considerable losses of radiogenic argon take place. Furthermore, it will be shown later that in the

case of diffusion the radiogenic argon content in a mineral should cease to be an asymptotic function of time and that a maximum value should occur at real ages and at the diffusion constant values given by Gentner *et al.* (1954) and Reynolds (1957). Therefore the argon content of a mineral should become indefinite.

It seems also rather improbable that, according to a theory proposed by Reynolds (1957), the activation energy of argon diffusion in feldspars should tend to diminish with decreasing temperature. If such were the case, the radiogenic argon losses should become considerable even at comparatively low values of absolute age. Figuratively speaking, feldspars in this case should resemble a leaking vessel, the fluid volume of which should be worthless for any quantitative speculations. Fortunately, however, such is not the case because some feldspars give argon-age values in excellent accordance with other methods and with geological considerations.

The present work has been accomplished at the Daghestan Branch of the Academy of Sciences of the U.S.S.R. since the beginning of 1957. Its purpose was to explore the causes and mechanism of radiogenic argon loss by some minerals and to find quantitative correction factors suitable for compensation for these losses. It never should be possible to fulfil the bulk of research work without a simple, rapid, and exact technique of radiogenic argon determination requiring only small amounts of geologic material. Our technique utilizes the mass-spectrometric isotope-dilution method developed at the Daghestan branch in 1953 and 1954 by Amirkhanoff *et al.* (1955) and substantially refined during the following years by Amirkhanoff and Brandt (1956).

#### *Extraction and Measurement Technique*

The apparatus for radiogenic argon determination consists of three main parts: (1) a closed volume called a reactor in which the fusion of sample and the sorption of expelled gases is accomplished, (2) the spike calibration device, and (3) the mass spectrometer.

The schematic of the reactor is shown in FIGURE 1. The vacuum-tight system consists of the stainless steel reactor (1), closed by a rubber-tightened steel inset with two electrical input-leads (2). The pumping system makes it possible to obtain pressures of the order of  $10^{-4}$  to  $10^{-5}$  mm. Hg. Inside the reactor a porcelain crucible with a molybdenum wire (diameter 0.8 to 1.0 mm.) heater is placed (3). The sample (1 to 5 gm.) is poured into the porcelain crucible among the windings of the molybdenum heater. Next to the crucible in the reactor is a calcium furnace (4) consisting of a porcelain tube (diameter 20 to 25 mm.) with several windings of 0.8 to 1.0 mm. molybdenum wire. Inside the porcelain tube 10 to 20 gm. of metallic calcium filings are poured. The calcium furnace and the crucible are covered with a screen (5) made of quartz or sheet steel.

In this same FIGURE 1 a diagram of the electric power supply is shown. The power consumption of the crucible heater is only a few hundred watts. With this fusion arrangement the temperature in the crucible reaches  $2000^{\circ}\text{C}$ . within 5 to 7 min., which is more than sufficient for complete fusion of the sample. The gas-purification procedure consists of several repeated warming

(to 800° to 900° C.) and cooling cycles of the calcium furnace. In the case of micas and feldspars the purification procedure takes from 30 to 40 min. In the case of glauconites, however, the procedure is somewhat more complicated.

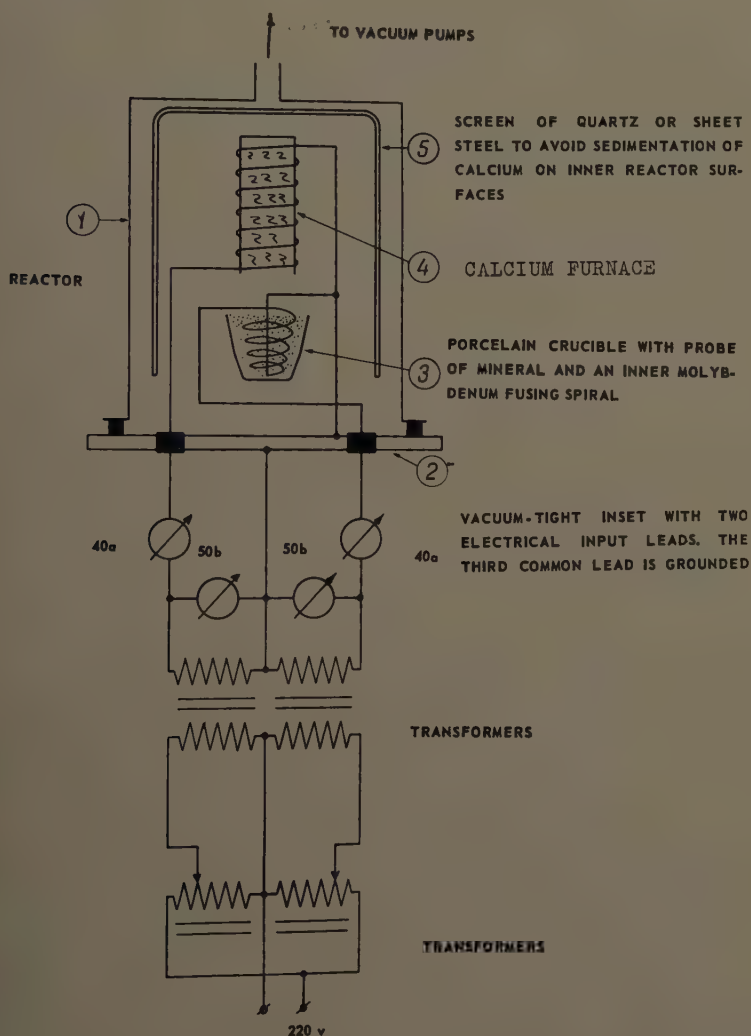


FIGURE 1. Schematic of the argon extraction and purification equipment.

After the gas pressure in the reactor has fallen to approximately  $10^{-3}$  mm. Hg, the quantitative mass-spectrometric determinations may be begun. A 20°, two-ray electromagnetic-type mass spectrometer is used, the first ray being tuned to the 36 mass, the second to the 40 mass. The ratio of the 36-mass channel to the 40-mass channel output voltages can be precisely measured by means of a potentiometer, thus giving the value of the appropriate isotope

ratio. The measuring procedure reduces to the determination of 3 isotope ratios  $K_1$  (or  $K_a$ ),  $K_2$ , and  $K_3$ . Thus is obtained a system of 3 equations, containing 3 unknown quantities: the amount of radiogenic argon in the given specimen  $X$  and the two contaminating, admitted, atmospheric argon isotopes  $Ar^{36}$  and  $Ar^{40}$ . The solution of this system enables us to determine  $X$  (it must be noted, that in all calculations the amount of the 38 isotope in atmospheric argon is irrelevant).

It is necessary to avoid discrimination effects in the ion source of the mass spectrometer.

First the isotope ratio of the spike used,  $K_1$ , is determined:

$$K_1 = \frac{Ar^{36}_s}{Ar^{40}_s} \quad (1)$$

The isotope ratio of atmospheric argon is:

$$K_a = \frac{Ar^{36}}{Ar^{40}} \quad (2)$$

It is proposed that this is identical to the isotope ratio of the contaminating argon in the reactor. If atmospheric argon is used as a spike we obviously have  $K_1 = K_a$ .

The second step is to determine the isotope ratio of the argon in the reactor after fusion and purification:

$$K_2 = \frac{Ar^{36}}{Ar^{40} + X} \quad (3)$$

Third is the isotope dilution process. The fundamental requirement of this method is that the isotopic consistency of the measured element differ from that of the spike. In the case of radiogenic-argon determinations this requirement is met automatically. Generally speaking we can use for dilution purposes argon of arbitrary isotope consistence. Therefore the argon content of the reactor is diluted by a known amount of the spike (normal mm.<sup>3</sup> reduced to *NTP*). This is accomplished by means of a normal volume, a McLeod gauge, and a thermometer. At actual reactor pressures ( $10^{-3}$  mm. Hg) the gas diffusion proceeds almost immediately and, in a few minutes, the argon mixture is ready for measurement. As a result we obtain the isotope ratio

$$K_3 = \frac{Ar^{36} + N^{36}}{Ar^{40} + N^{40} + X} \quad (4)$$

where  $N$  is the amount of the spike added.

From 1, 2, 3, and 4 the unknown  $X$  may be easily determined:

$$X = N \frac{(K_1 - K_3)(K_a - K_2)}{K_a(K_3 - K_2)(K_1 + 1)} \quad (5)$$

In the case of atmospheric argon spike, as it is done in our measurements, 5



reduces to

$$X = N \frac{K_a - K_3}{K_3 - K_2} \left( 1 - \frac{K_2}{K_a} \right) \quad (6)$$

(we assume  $K_a \ll 1$ ).

The same equipment enables us to determine the helium and the argon content of the specimens simultaneously. In this case a mixture of  $\text{He}^4$  ( $\beta$  parts) and of atmospheric argon (1 to  $\beta$  parts) is used as a spike. The preparation procedure of the system is the same as in the case above. After determining  $K_2$ , one of the mass spectrometer channels is tuned to  $\text{He}^4$ . The inlet valve of the ion source is then slightly opened, and the reading of the output voltmeter, corresponding to the  $\text{He}^4$  content in the reactor ( $\alpha_1$ ) is taken. Then, with the inlet valve open, a known amount of  $\text{He}^4$  is introduced into the reactor, thereby obtaining an output reading of the voltmeter  $\alpha_2$  as the diffusion of helium in the reactor occurs very fast. The unknown amount of helium in the reactor then may be readily obtained by the relation:

$$\text{He}^4 = N \cdot \beta \frac{\alpha_1}{\alpha_2 - \alpha_1} \quad (7)$$

Finally the mass spectrometer is tuned over again to  $\text{Ar}^{36}$  and  $\text{Ar}^{40}$  and the determination of  $K_3$  is made. During this determination the mass spectrometer must be checked several times for a correct value of  $K_a$ . Obviously this technique can be generalized to the determination of more than two gas components in the reactor provided an adequate gas-mixture is used as a spike. The accuracy of measurements is thereby of course slightly affected, but the corresponding correction factors can easily be found.

#### *The Accuracy of Radiogenic-Argon Determinations*

In order to compare the techniques used in this work with other varieties of isotope-dilution method, the question of relative errors involved must be studied.

Equation 5 gives the argon content  $X$  as a function of the corresponding isotope ratios and of the amount of the spike added, that is

$$X = f(N, K_1, K_2, K_3, K_a) = N\phi(K_1, K_2, K_3, K_a) \quad (8)$$

We make use of the well-known relative error formula:

$$E = \frac{\Delta X}{X} = \frac{1}{N\phi} \left[ \Delta N \left( \frac{\partial(N\phi)}{\partial N} \right) + \Delta K_1 \left( \frac{\partial(N\phi)}{\partial K_1} \right) + \Delta K_2 \left( \frac{\partial(N\phi)}{\partial K_2} \right) + \Delta K_3 \left( \frac{\partial(N\phi)}{\partial K_3} \right) + \Delta K_a \left( \frac{\partial(N\phi)}{\partial K_a} \right) \right]$$

Here  $\Delta K_i$  denotes the absolute errors of mass-spectrometric determinations of the corresponding isotope ratios. Assuming  $\Delta K_1 = \Delta K_2 = \Delta K_3 = \Delta K_a = \Delta$ , then

$$E = \frac{\Delta X}{X} = \frac{\Delta N}{N} + \frac{\Delta}{\phi} \left[ \left( \frac{\partial \phi}{\partial K_1} \right) + \left( \frac{\partial \phi}{\partial K_2} \right) + \left( \frac{\partial \phi}{\partial K_3} \right) + \left( \frac{\partial \phi}{\partial K_a} \right) \right] \quad (9)$$

Taking the private derivatives of **8**, the final form of the relative error expression is obtained:

$$E = \frac{\Delta X}{X} = \frac{\Delta N}{N} + \Delta \left[ \left( \frac{1 - K_3}{(1 + K_1)(K_1 - K_3)} \right) + \left( \frac{K_a - K_3}{(K_3 - K_2)(K_a - K_2)} \right) + \left( \frac{K_1 - K_2}{(K_3 - K_2)(K_1 - K_3)} \right) + \left( \frac{K_2}{K_a(K_a - K_2)} \right) \right] \quad (10)$$

Now it is seen that this expression has several poles, that is, turns to infinity at some values of the variables.  $K_a$  and  $K_1$  must be taken as constants.  $K_2$  varies from 0 to  $K_a$  depending on the amount of the contaminating atmospheric argon.  $K_3$  can vary from  $K_2$  and  $K_1$  and depends on the amount of spike added. The error of argon determinations is infinitely high at three values of the variables:

(1)  $K_2 = K_a$ , if the amount of radiogenic argon is small compared with the atmospheric contamination. In this sense the measurement of argon-poor specimens is equivalent to excessive sorbtion or leakage of atmospheric argon. The requirement  $K_2 < K_a$  is independent of isotope dilution and is the *conditio sine qua non* for all the subsequent manipulations.

(2)  $K_2 = K_3$ , if the amount of spike added is small compared with the argon mixture in the reactor. It may be also that the dilution is carried out with a spike of atmospheric consistence and  $K_2$  differs but slightly from  $K_a$ .

(3)  $K_1 = K_3$ , if the amount of spike added is too large.

The last two conditions give evidence that there must exist an optimum degree of dilution corresponding to a minimum value of  $E$ . In deducing the expression for this optimum two conceptions must be defined: the degree of dilution  $B = N/X$  and the degree of contamination  $G = Ar/X$ . It is assumed further that  $1 \pm K_a \cong 1$ , then we may write:

$$K_2 = \frac{K_a G}{G + 1}; \quad K_3 = \frac{K_a G(1 + K_1) + K_1 B}{G(1 + K_1) + B + 1 + K_1} \quad (11)$$

Combining **11** with **10** we obtain:

$$E = \frac{\Delta N}{N} + \Delta \left[ \left( \frac{G + B + 1}{(1 + K_1)[G(K_1 - K_a) + K_1]} \right) + \left( \frac{(G + 1)^2[B(K_a - K_1) + K_a(1 + K_1)]}{K_a B[G(K_1 - K_a) + K_1]} \right) + \left( \frac{[(G + 1)(1 + K_1) + B]^2}{B(1 + K_1)[G(K_1 - K_a) + K_1]} \right) + \left( \frac{G}{K_a} \right) \right] \quad (12)$$

Because of the somewhat complicated form of **12** we shall restrict analysis to some private cases of practical importance.

(1) Zero air contamination ( $G = 0$ ) with atmospheric argon used as a spike ( $K_1 = K_a$ ):

$$E_{1,1} = \frac{\Delta N}{N} + \frac{\Delta}{K_a} \left[ B + 1 + \frac{1}{B} + \frac{(B + 1)^2}{B} \right]$$

Equaling ( $\partial E_{1,1}/\partial B$ ) zero we obtain  $B_{opt} = 1$ .

(2) Zero air contamination ( $G = 0$ ) with argon highly enriched by the 36 isotope used as spike ( $K_1 = 1$ ):

$$E_{1,2} = \frac{\Delta N}{N} + \Delta \left[ B + 2.5 + \frac{2}{B} + \left( \frac{2}{B} - \frac{1}{K_a} \right) \right]$$

Optimum dilution  $B_{opt} = 2$ .

(3) Considerable atmospheric argon contamination ( $G = 1$ ) with atmospheric argon used as spike ( $K_1 = K_a$ ).

$$E_{2,1} = \frac{\Delta N}{N} + \frac{\Delta}{K_a} \left[ 2B + 5 + \frac{8}{B} \right]$$

Optimum dilution  $B_{opt} = 2$ .

(4) Considerable atmospheric argon contamination ( $G = 1$ ) with argon highly enriched by the 36 isotope used as spike ( $K_1 = 1$ ).

$$E_{2,2} = \frac{\Delta N}{N} + \Delta \left[ \frac{B}{2} + 2.5 + \frac{4}{B} + \frac{1}{K_a} + \left( \frac{4}{B} - \frac{2}{K_a} \right) \right]$$

Optimum dilution  $B_{opt} = 4$ .

Thus the optimum conditions in the isotope dilution method are realized if the amount of measured argon is commensurable with the amount of diluting spike added. Rigorously speaking, the measuring procedure therefore should be a subject of successive approximation. Fortunately, in the hands of well-trained personnel, the first approach gives fairly satisfactory results.

In FIGURE 2 the curves of  $E_{i,k}$  are plotted against  $B$ . In calculating the following numerous values of the parameters were taken into account:  $(\Delta N/N) = 1$  per cent,  $\Delta = 10^{-5}$ ,  $K_a = 3.4 \times 10^{-3}$ . From these curves we may draw the following conclusions:

(1) The relative error considerably depends on air contamination. All possibilities of leakage in the apparatus therefore must be accurately removed. In spite of this, there nearly always exists a background of atmospheric argon in the system, for adsorbed atmospheric argon is often very strongly bounded to the surfaces of minerals and rocks and is not to be removed by low-temperature preheating. A more intensive preheating would be impracticable because of the increasing probability of radiogenic argon losses.

(2) The relative error substantially decreases if a spike enriched with the 36 isotope is used (two- to threefold). The influence of the degree of dilution becomes negligible, and the working conditions become at first sight more favorable. It must be noted, however, that the measuring procedure becomes in this case somewhat more complicated as the apparatus becomes highly sensitive

to the least tracks of atmospheric argon leakage. Tracks of atmospheric or spike argon that may remain on the walls of the apparatus due to sorption may introduce considerable errors in the determination of successive isotope ratios.

Now we shall consider two of the most widespread methods: (1) the volumetric method of radiogenic argon determination by means of a McLeod gauge with subsequent mass-spectrometric control of atmospheric contamination and (2) the isotope-dilution techniques using an  $\text{Ar}^{38}$  monoisotope spike.

In the first case the extracted argon is usually checked for the  $\text{Ar}^{36}/\text{Ar}^{40}$  ratio. If there is no atmospheric argon contamination, this ratio becomes zero. Such cases, however, are extremely rare as the  $\text{Ar}^{36}/\text{Ar}^{40}$  ratio usually has a finite value. Furthermore, if the argon extraction apparatus and the mass spectrometer are located distinctly, the radiogenic argon may be subjected to additional contamination in the course of communicating it to the mass spectrometer.

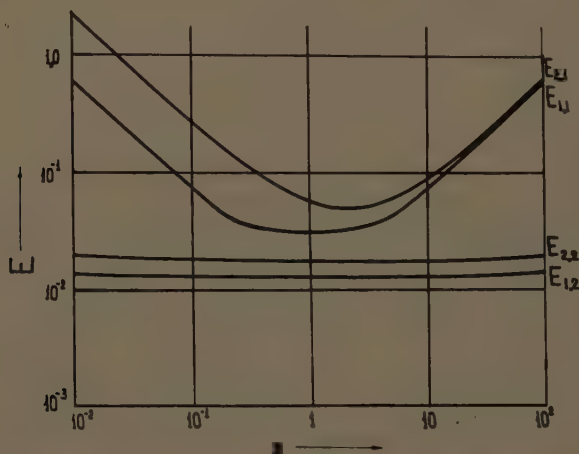


FIGURE 2. Argon-determination error as a function of the degree of isotopic dilution.

To avoid isotopic discrimination in the ion source of the mass spectrometer, the procedure must involve the measurement of at least 2 isotope ratios:

$$K_a = \frac{\text{Ar}^{36}}{\text{Ar}^{40}} \quad \text{and} \quad K_1 = \frac{\text{Ar}^{36}}{\text{Ar}^{40} + X}$$

These 2 equations can be solved with respect to  $X$ :

$$X = \text{Ar} \frac{K_a - K_1}{K_a(1 + K_1)} \quad (13)$$

(Ar-argon amount measured by the McLeod Gauge).

The general error expression for this case becomes:

$$E = \frac{1}{X} \left[ \Delta \text{Ar} \left( \frac{\partial X}{\partial \text{Ar}} \right) + \Delta K_a \left( \frac{\partial X}{\partial K_a} \right) + \Delta K_1 \left( \frac{\partial X}{\partial K_1} \right) \right]$$

After elementary transformations and taking the corresponding private derivatives we finally obtain:

$$E = \frac{\Delta \text{Ar}}{\text{Ar}} + \Delta \left[ \left( \frac{K_1}{K_a(K_a - K_1)} \right) + \left( \frac{1}{(1 + K_1)(K_a - K_1)} \right) \right] \quad (14)$$

We see that in this case the error varies from  $(\Delta \text{Ar}/\text{Ar}) + (\Delta/K_a)$  at  $K_1 = 0$ , that is at zero atmospheric contamination, to  $\infty$  at  $K_a = K_1$ , if considerable contamination takes place. Considerable and indefinite additional errors may arise due to the procedure of communicating the probe to the mass spectrometer and to incomplete chemical purification in the apparatus. Obviously this procedure cannot be regarded a reliable one from the modern point of view.

Use of the monoisotope  $\text{Ar}^{38}$  spike involves the following isotope ratios:

$$n_1 = \frac{\text{Ar}^{36}}{\text{Ar}^{40}}; n_2 = \frac{\text{Ar}^{38}}{\text{Ar}^{40}}; n_3 = \frac{\text{Ar}^{36}}{\text{Ar}^{38} + \text{N}^{38}}; n_4 = \frac{\text{Ar}^{38} + \text{N}^{38}}{\text{Ar}^{40} + X};$$

where  $\text{Ar}^{36,38,40}$  are the isotopes of the atmospheric argon, N is the spike, and X is the radiogenic argon.

We must emphasize that in this technique the mass spectrometer must be twice tuned over from the 36 and 38 to the 38 and 40 isotopes. This complication can be regarded as an additional source of error as compared with the technique using the  $\text{Ar}^{36}/\text{Ar}^{40}$  spike.

The amount of radiogenic argon is given by:

$$X = \text{N}^{38} \frac{n_1 - n_3 n_4}{n_4(n_1 - n_2 n_3)} \quad (15)$$

The relation for the relative error shall be:

$$E = \frac{\Delta \text{N}}{\text{N}} + \Delta \left[ \left( \frac{n_3(n_4 - n_2)}{(n_1 - n_2 n_3)(n_1 - n_3 n_4)} \right) + \left( \frac{n_3}{n_1 - n_2 n_3} \right) + \left( \frac{n_1(n_2 - n_4)}{(n_1 - n_2 n_3)(n_1 - n_3 n_4)} \right) + \left( \frac{n_1}{n_4(n_1 - n_3 n_4)} \right) \right] \quad (16)$$

Equation 16 brings us to the following conclusions:

(1) The term  $(\Delta \text{N}/\text{N})$  is equivalent to the corresponding term in the atmospheric argon-dilution technique.

(2) The error turns to infinity at  $n_1 - n_2 n_3 = 0$ , or  $[\text{Ar}^{38}/(\text{Ar}^{38} + \text{N}^{38})] = 1$ , meaning that measurements should not be carried out if the amount of spike added is too small.

(3) The error turns to infinity if  $n_4 = \infty$  (or  $n_3 = 0$ ), that is if the amount of spike added is too large.

(4) The error turns also to infinity at  $n_1 - n_3 n_4 = 0$ , or  $[\text{Ar}^{40}/(\text{Ar}^{40} + X)] = 1$ , that is, in the case of extremely large atmospheric argon contamination.

From the introductory remarks to this paper it follows that there always should exist an optimum degree of isotope dilution, as was the case with the atmospheric argon-dilution technique.

Hence we see that the procedure using the 38 monoisotope is highly analogous



to the atmospheric argon-dilution technique. The expressions developed do not show any advantages of the monoisotope-dilution technique. Furthermore there exists a definite probability of additional errors due to the fact that the number of tuning-over manipulations in the last case is doubled as compared with the atmospheric argon-dilution technique.

The calculations developed above do not contain any information about the threshold of sensitivity of the apparatus, that is, the minimum measurable amount of radiogenic argon. The treatment of this problem shows, however, (Amirkhanoff and Brandt, 1956) that it depends chiefly upon the absolute sensitivity of the mass spectrometer and the degree of atmospheric argon contamination.

### *The Mechanism of Radiogenic Argon Loss by Different Minerals*

*The diffusion of radiogenic argon in minerals.* To explain the losses of radiogenic argon the hypothesis of diffusion into the surrounding medium was proposed by several authors. Apparently the first attempt at a quantitative treatment of argon losses by minerals based on diffusion was undertaken by Gentner *et al.* (1953). The diffusion constant  $D$  obtained by these authors for sylvite was of the order of  $10^{-20}$  cm.<sup>2</sup>/sec. There arise some doubts however, not only because of this somewhat large value for  $D$ , but also because the authors use an incorrect form of diffusion equation. Their basic equation has the form:

$$\frac{\partial C}{\partial t} = D\Delta C - \lambda C + \lambda_0 C_{K_0},$$

where  $C_{K_0}$  is the concentration of  $K^{40}$  at  $t = 0$  and  $C$  is the radiogenic-argon concentration found experimentally. Following this equation, the rate of radiogenic argon production depends on the actual concentration; that is,  $C$  is a function of coordinates. The correct equation must involve the so-called source-function, as shown by Amirkhanoff *et al.* (1958).

The radiogenic argon diffusion was investigated also by Reynolds (1957). The diffusion constants for lepidolites and feldspars were determined. The diffusion was supposed to be isotropic, spherically symmetrical, and the concentration of radiogenic argon at the surface of the mineral was taken to be zero. The calculations were based on the formula:

$$f = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D t}{a^2}\right),$$

where  $f$  is the fraction of radiogenic argon lost by the mineral at a given preheating temperature,  $a$  is the grain radius and  $t = 48$  hrs. The results of  $D$  measurements for lepidolite are not shown. The true values of  $D$  for feldspars are thought to be obtainable from an extrapolation procedure (FIGURE 3). The experimental  $D$  versus  $1/T$ -plots *BB* are prolonged toward an arbitrary initial temperature line, which they cross in point *F*, believed to demark the true value of  $D$  at room temperature being  $> 10^{-19}$  cm.<sup>2</sup>/sec. Our opinion is that the interpretation of experimental results is in this case somewhat incorrect. The rigorous scientific consciousness of the author and comparison with

our own results lead us to propose another treatment. Indeed, Reynolds mentions that at 600° C. an extremely low value of  $D$  was obtained and, believing this point to be erroneous, the author omitted it in his curve. If this point is plotted, a curve close to  $AA$  in FIGURE 3 is obtained. It will be shown later that, in order to explain the high values of  $D$  at lower temperatures, we are to suppose a discontinuity in the vicinity of 600° C. due to phase transitions occurring at these temperatures. Consequently, the  $D$  value at room temperatures is expectably much smaller than that estimated by Reynolds.

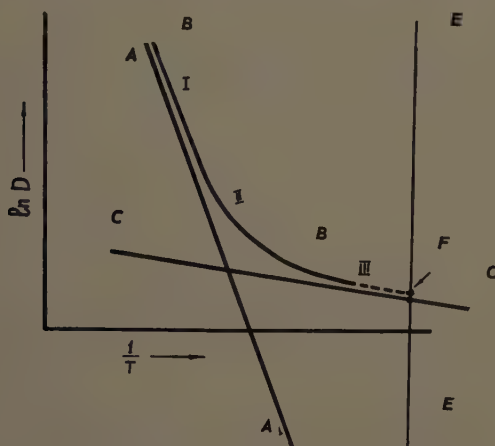


FIGURE 3. The knee on the temperature curve of  $D$ .

What values of  $D$  are to be regarded as the most probable? We shall use the spherical diffusion formula taking into consideration the radioactive decay:

$$\text{Ar}^{40} = \frac{\lambda_e}{\lambda} K_0^{40} \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \left[ \frac{\exp\left(-\frac{n^2 \pi^2 D t}{a^2}\right) - \exp(-\lambda t)}{1 - \left(\frac{n\pi}{a}\right)^2 \frac{D}{\lambda}} \right] \quad (17)$$

The plot of  $\text{Ar}^{40}/K_0^{40}$  against  $t$  at different values of  $Da^{-2}/\lambda$  is shown in FIGURE 4.

It should be mentioned that in the case of micas the diffusion cannot be regarded as spherically symmetrical. We neglect the diffusion flux perpendicular to the cleavage planes and consider the diffusion flux taking place parallel to the cleavage planes only. The diffusion equation takes the form:

$$\text{Ar}^{40} = \frac{\lambda_e}{\lambda} K_0^{40} \sum_{n=1}^{\infty} \frac{4 \left[ \exp\left(-\frac{(\mu_0^n)^2 D \tau}{a^2}\right) - \exp(-\lambda \tau) \right]}{(\mu_0^n)^2 \left[ 1 - \left(\frac{\mu_0^n}{a}\right)^2 \frac{D}{\lambda} \right]} \quad (18)$$

Here  $\text{Ar}^{40}$  is the radiogenic argon content of the mineral,  $K_0^{40}$  its initial  $K^{40}$  content,  $\mu_0^n$  the  $n$ th root of the Bessel function of the first kind and zero order,  $a$

the radius of the mica sheet, and  $\tau$  the time of existence of the mineral. The somewhat different form of Equations 17 and 18 of course changes nothing in our considerations of diffusion.

In laboratory research on diffusion it is impossible to use geological time intervals. Therefore we intensify the process, which is accomplished by studying the diffusion at higher temperatures. The preheating time of the mineral

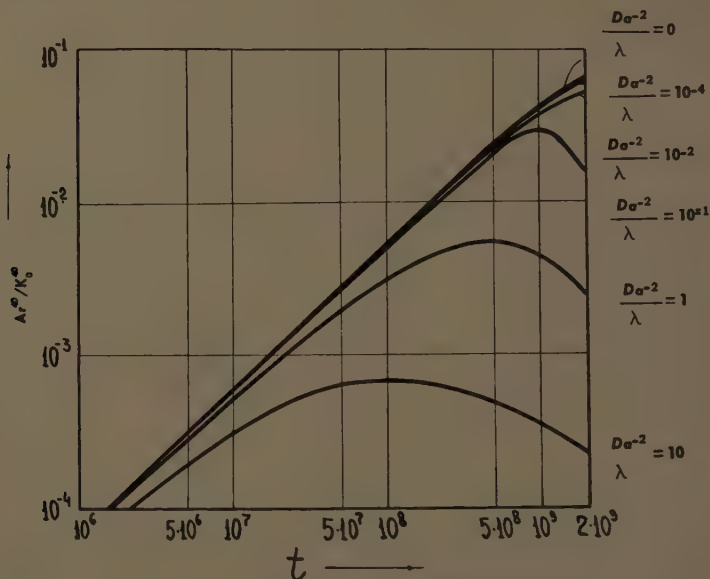


FIGURE 4. Dependence of  $\text{Ar}^{40}/\text{K}_0^{40}$  upon  $Da^{-2}/\lambda$ .

sample ( $t$ ) is much smaller than  $\tau$ ; thus we may neglect the amount of radiogenic argon created during our laboratory procedures. Equation 18 becomes:

$$\frac{\text{Ar}_t^{40}}{\text{Ar}_0^{40}} = \sum_{n=1}^{\infty} \frac{4}{(\mu_n^n)^2} \exp\left(-\frac{(\mu_n^n)^2 D_\tau t}{a^2}\right) \quad (19)$$

where  $\text{Ar}_t^{40}$  is the radiogenic argon content after preheating the sample at a temperature  $T$  during the time interval  $t$ ;  $\text{Ar}_0^{40}$  is the initial argon content before preheating, and  $D_\tau$  is the diffusion constant at a temperature  $T$ .

In the case of feldspars and sylvites the isotropic diffusion formula was used:

$$\frac{\text{Ar}_t^{40}}{\text{Ar}_0^{40}} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_\tau t}{a^2}\right) \quad (20)$$

In FIGURE 5 the radiogenic argon leakage curves for phlogopite are shown (grain size  $< 0.053$  mm.;  $\text{Ar}_0^{40} = 1.070$  mm.<sup>3</sup>/gm.). Examining the curves of FIGURE 5, it is seen that they fall into two distinct types.

The curves of the first type were obtained at temperatures 150 to 600° C. In this case the radiogenic argon escapes the mineral during the first 30 min.

of preheating. During subsequent preheating the argon content remains constant. This case will be treated later in this paper.

The curves of the second type at temperatures 750 to 900° C. show a monotonic diminution of radiogenic argon during preheating. It must be emphasized however that in this case the curves tend to a lower limit, which is found by intersection of the horizontal part of the 900° curve with the ordinate axis (in our case this limit is 0.040 mm.<sup>3</sup>/gm.).

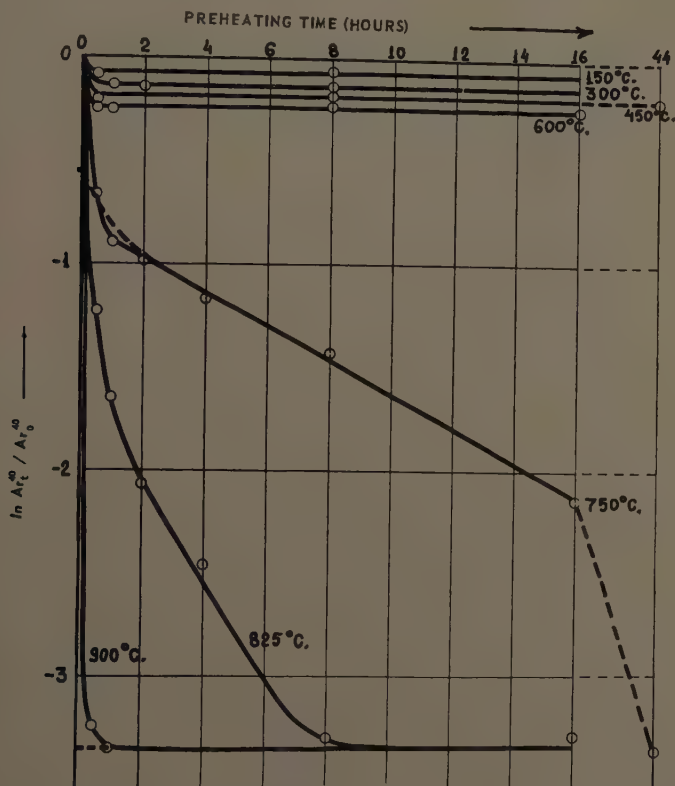


FIGURE 5.  $\text{Ar}^{40}$  leakage from phlogopite (grain size  $< 0.053$  mm.) as a function of preheating time at different temperatures.

Thus it is natural to suppose that the radiogenic argon atoms in mica exist in three different states or positions and that their migration is controlled by three different mechanisms. In studying them we must discover first the distribution of argon between these three states.

The third state, as already shown, contains 0.040 mm.<sup>3</sup>/gm. radiogenic argon.

The amounts of argon in the first and second states were determined as follows. A set of  $D$  curves was calculated from Equation 19 using an average value of 0.020 mm. This set of calculated curves is shown in FIGURE 6. In imposing them on the experimental curves and in moving them in the direction

of the ordinate axis, we chose a theoretical curve the slope of which coincided with that of the experimental curve for  $750^{\circ}\text{C}$ . The intersection of the theoretical curve chosen with the ordinate axis determined the amounts of radiogenic argon in the second and first states ( $\text{Ar}_{0\text{I}}^{40} = 0.450 \text{ nmm.}^3/\text{gm.}$ ,  $\text{Ar}_{0\text{II}}^{40} = 0.580 \text{ nmm.}^3/\text{gm.}$ ) as indicated by the dotted line in FIGURE 5. Its slope determines the diffusion constant  $D$ .

The argon-leakage curves due to the second state are shown in FIGURE 7. The curve for  $900^{\circ}\text{C}$ . could not be plotted as the rate of argon leakage for this

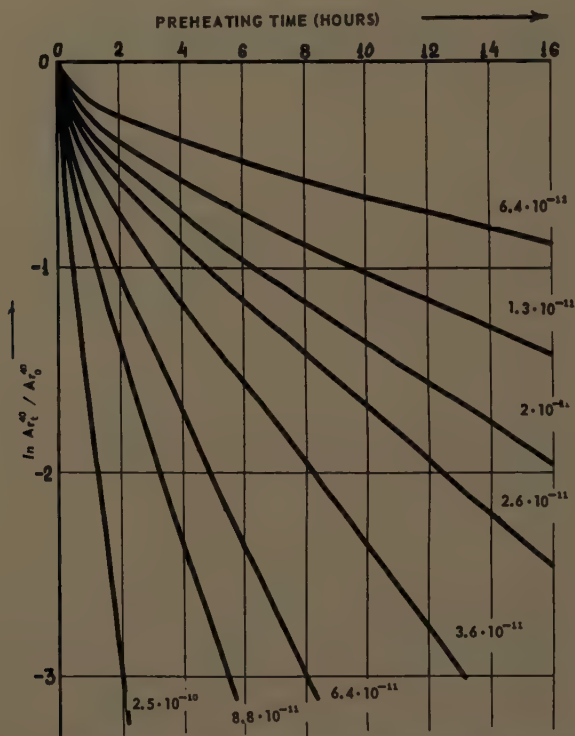


FIGURE 6. A set of theoretical  $\text{Ar}^{40}$  diffusion curves for micas ( $a = 0.02 \text{ mm.}$ ).

temperature is too rapid to allow calculation of  $D$  at our minimum time interval (0.5 hours).

The values of  $D_T$ , determined by this method, are  $1.9 \times 10^{-11} \text{ cm.}^2/\text{sec.}$  and  $9.5 \times 10^{-11} \text{ cm.}^2/\text{sec.}$  for  $750^{\circ}$  and  $825^{\circ}\text{C}$ . respectively. The corresponding activation energy equals 48,000 cal./mol. From these values of  $E$  and  $D_T$  we obtain the diffusion constant related to  $300^{\circ}\text{K}$  as equal to  $5.5 \times 10^{-36} \text{ cm.}^2/\text{sec.}$

The argon-leakage curves for two samples of feldspars are shown in FIGURES 8 and 9. Grain sizes of 0.053 to 0.105 mm. were used for the analysis. For the purpose of quantitative treatment a set of diffusion curves was calculated for the grain size  $a = 0.04 \text{ mm.}$  according to Equation 20 and plotted in the same coordinate system as above.



From FIGURE 8 (feldspar sample N35,  $\text{Ar}_0^{40} = 0.962 \text{ mm.}^3/\text{gm.}$ ) it may be seen that the leakage curves have horizontal parts with zero slope of considerable lengths at  $800^\circ$  and  $1100^\circ \text{ C.}$  despite Equation 20. Furthermore, the slope

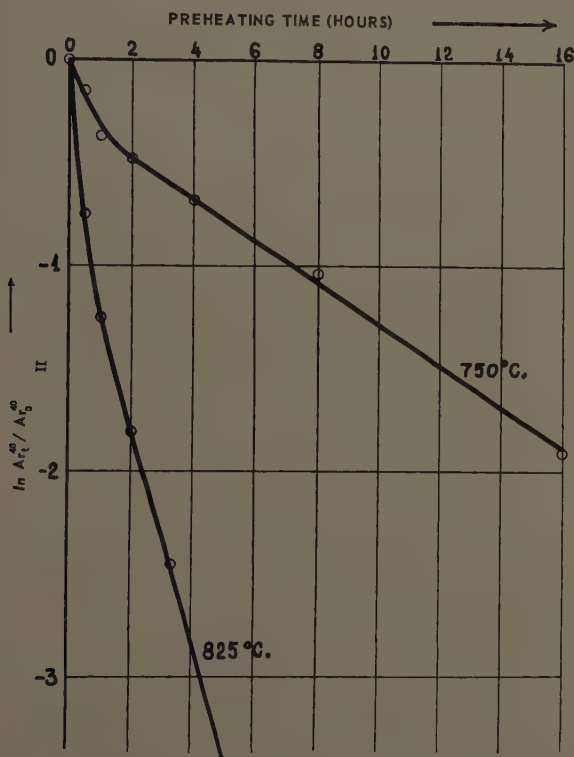


FIGURE 7.  $\text{Ar}^{40}$  leakage curves for the second state of  $\text{Ar}^{40}$  in phlogopite.

of the curves does not increase monotonically, as would be the case according to the equation

$$D = D_0 \exp\left(-\frac{E}{RT}\right), \quad (21)$$

but instead varies periodically.

In order to clarify the nature of the horizontal parts just mentioned, a leakage curve of the sample N35 feldspar at  $800^\circ \text{ C.}$  for a much finer grain size, obtained by crushing the fraction 0.053 to 0.105 mm. in an agate mortar, was determined (the points of this curve are indicated by crosses in FIGURE 8). It is seen that the curve remains horizontal and that this feature is independent of the grain size and obviously depends only on the crystalline structure. The beginning of the horizontal part of the curve approaches the ordinate axis in accordance with the role of the parameter  $D/a^2$  in Equation 20. The phenomenon taking place at  $800^\circ$  and  $1100^\circ \text{ C.}$  may be therefore seen as a rapidly damped

diffusion, exhausting the content of radiogenic argon in a definite state and determined by some characteristic values of  $E$  and  $D_0$ . Accepting the terminology of physical chemistry of polyphase systems, we may denote these zero slope curves as spinodals. The intersection of the spinodal with the ordinate axis determines the content of radiogenic argon in each state (or phase). It should be noted that, despite the statement of Gentner and Kley (1957), the initial argon content of the sample remained constant after crushing.

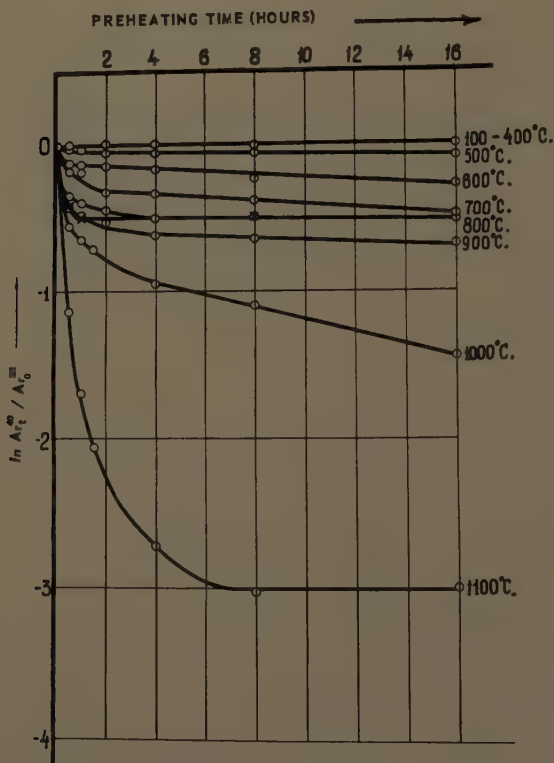


FIGURE 8.  $\text{Ar}^{40}$  leakage curves at different temperatures for the feldspar specimen N35.

Therefore the interpretation of the experimental curves should be stated in terms of the radiogenic argon belonging to each state (or phase) separately.

As may be seen in FIGURE 8, sample N35 has three phases containing the following amounts of radiogenic argon: Phase I =  $t < 800^\circ \text{C}$ .,  $\text{Ar}_{0\text{I}}^{40} = 0.370 \text{ nmm.}^3/\text{gm.}$ ; Phase II =  $800^\circ \text{C.} < t < 1100^\circ \text{C.}$ ,  $\text{Ar}_{0\text{II}}^{40} = 0.546 \text{ nmm.}^3/\text{gm.}$ ; Phase III =  $t > 1100^\circ \text{C.}$ ,  $\text{Ar}_{0\text{III}}^{40} = 0.046 \text{ nmm.}^3/\text{gm.}$  The results of such a treatment are shown in FIGURE 10 (full lines = Phase I, dotted lines = Phase II).

In the same way the argon content of sample N65 may be divided into three phases. To find the phase boundaries, we proceed as in the case of phlogopite:

it is assumed that the rectilinear part of the curve at 700° C. corresponds to the argon leakage from Phase II only, whereas the analogous part of the curve at 1100° C. corresponds to Phase III only. The characteristic feature of this feldspar lies in the presence of a "zero" phase, the radiogenic argon of which escapes at 400° C. during the first minutes of preheating. This phenomenon is obviously highly analogous to the mechanism of argon escape from phlogopite at 150 to 600° C.

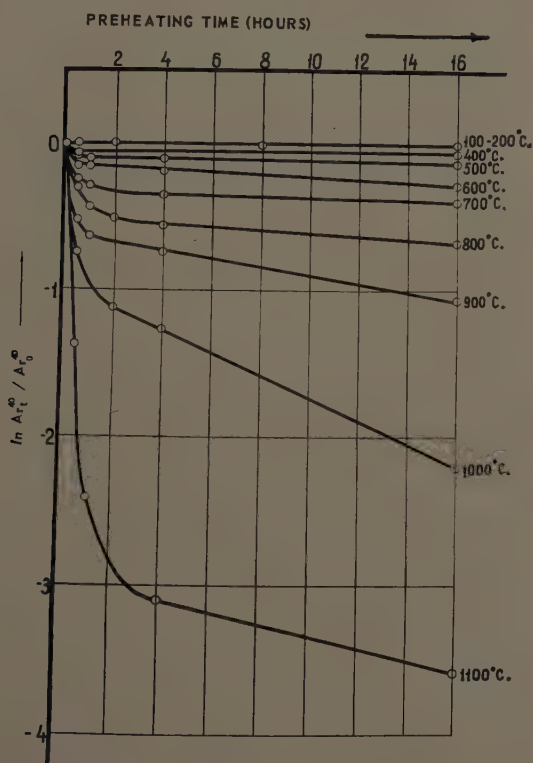


FIGURE 9.  $\text{Ar}^{40}$  leakage curves at different temperatures for the feldspar specimen N65.

The radiogenic argon contents of the several phases are as follows: Zero phase =  $t < 400^\circ \text{C.}$ ,  $\text{Ar}_{00}^{40} = 0.060 \text{ nmm.}^3/\text{gm.}$ ; Phase I =  $400^\circ < t < 700^\circ \text{C.}$ ,  $\text{Ar}_{01}^{40} = 0.206 \text{ nmm.}^3/\text{gm.}$ ; Phase II =  $600^\circ < t < 1100^\circ \text{C.}$ ,  $\text{Ar}_{011}^{40} = 0.659 \text{ nmm.}^3/\text{gm.}$ ; Phase III =  $t > 1100^\circ \text{C.}$ ,  $\text{Ar}_{0111}^{40} = 0.067 \text{ nmm.}^3/\text{gm.}$  The results of calculation are plotted in FIGURE 11.

The fact that the slope of curves in FIGURES 10 and 11 increases monotonically allows us to treat them in terms of Equations 20 and 21 and justifies the presumptions made. The values of  $D_T$  were found by imposing a set of calculated diffusion curves. The values of  $E$  and  $D_{300^\circ \text{K.}}$  were obtained using two adjacent  $D_T$  and Equation 21. The results are given in TABLE 1.

It may be seen from TABLE 1 that each phase is in fact determined by its

characteristic activation energy. The number and configuration of phases in the two samples studied are different, and these two cases obviously do not exhaust the wide variety of possible real feldspars.

It should be noted that the data obtained thus far for phlogopite and feldspar per se do not give any information as to the mechanism of argon diffusion. Therefore complementary experiments are to be undertaken for this purpose.

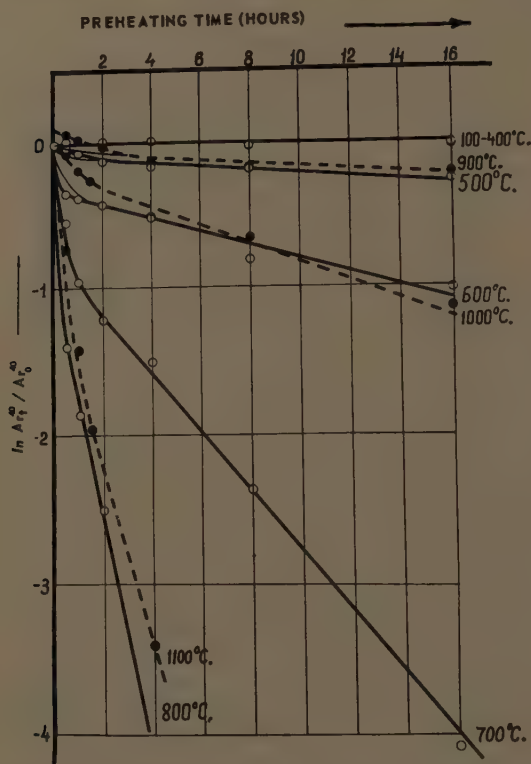


FIGURE 10.  $\text{Ar}^{40}$  leakage curves for the first and second  $\text{Ar}^{40}$  states in feldspar N35.

It is practical to begin the study of the mechanism of radiogenic argon diffusion from the most structurally simple mineral, sylvite, having a cubical symmetry system.

The radiogenic argon leakage curves for two specimens of sylvite, arbitrarily called red and rosy, are shown in FIGURE 12 ( $a$  = red,  $b$  = rosy). The values of  $D$  and  $E$  denoted at the corresponding curves were determined as above. In FIGURE 12a we see that the radiogenic argon diffusion takes place in the temperature interval 300° to 500° C. (at 500° C. all of the radiogenic argon escapes during the first hour of preheating). The activation energy is approximately constant in this interval and equals 37 to 47 kcal./mole ( $\sim 2$  ev). A more complicated case is found in the rosy sample (FIGURE 12b). First, low temperature losses of argon at 300° C. are observed, as it was in the cases of

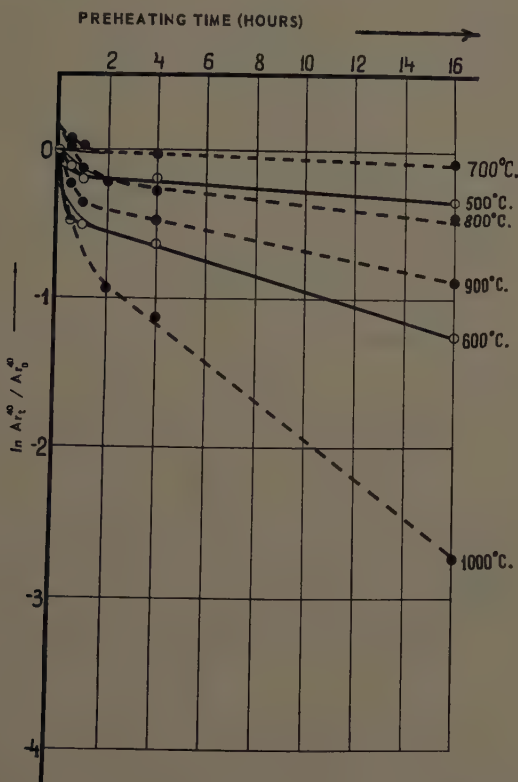
FIGURE 11.  $\text{Ar}^{40}$  leakage curves for the first and second  $\text{Ar}^{40}$  states in feldspar N65.

TABLE 1  
DIFFUSION CONSTANTS  $D_T$  AND ENERGIES OF ACTIVATION IN DIFFERENT  
PHASES OF FELDSPAR SAMPLES N35 AND N65

	Phase	$t^\circ \text{C. of preheating}$	$D_T \text{ cm}^2/\text{sec.}$	$E \text{ cal./mol.}$	$E \text{ average}$	$D_{900^\circ \text{K. cm}^2/\text{sec.}}$
N35	I	500	$10^{-12}$			
		600	$1.4 \cdot 10^{-11}$	35,600	33,600	$1.5 \cdot 10^{-27}$
		700	$9.5 \cdot 10^{-11}$	32,600		
		800	$4.5 \cdot 10^{-10}$	32,700		
	II	900	$8.0 \cdot 10^{-13}$		98,000	$2.0 \cdot 10^{-65}$
		1000	$1.8 \cdot 10^{-11}$	93,000		
		1100	$3.5 \cdot 10^{-10}$	103,000		
N65	I	500	$10^{-12}$		36,500	$6.0 \cdot 10^{-29}$
		600	$1.5 \cdot 10^{-11}$	36,500		
	II	700	$5.0 \cdot 10^{-13}$		39,000	$1.5 \cdot 10^{-32}$
		800	$3.0 \cdot 10^{-12}$	37,300		
		900	$1.5 \cdot 10^{-11}$	40,500		
		1000	$6.0 \cdot 10^{-11}$	39,100		



phlogopite and feldspar N65. Second, although the activation energy in the temperature interval 300 to 500° C. is of the same order as the case of red sylvite, for the interval 500 to 600° C. its value decreases to 16 kcal./mole (0.7 ev), which disagrees with the general principles of heat activation. It is therefore necessary to suppose that in this temperature interval the mechanism of argon diffusion changes and differs at 600° C. from that at lower temperatures, that is, analogous to that of feldspars, the argon leakage occurs from the subsequent phase. Thus the activation energy may not be calculated from values of  $D$  due to different mechanisms of diffusion. Given  $E = 47$  kcal./mole, we obtain  $D_{300^\circ \text{K.}} \cong 10^{-30}$  cm.<sup>2</sup>/sec. for both sylvites.

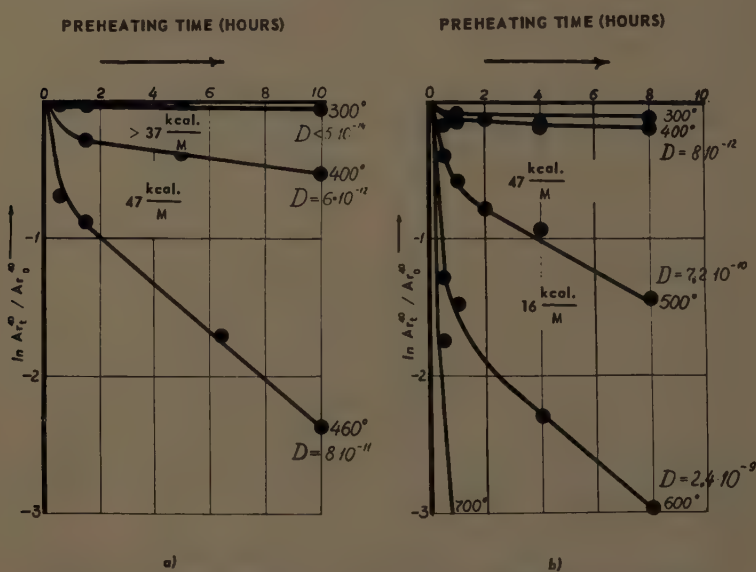


FIGURE 12.  $\text{Ar}^{40}$  leakage curves from sylvite at different temperatures.

It is well known that the self-diffusion of alkali ions and the electrical conductivity in alkali-halide crystals obey the Nernst-Einstein relation. The activation energy of both falls with decreasing temperatures (Gruner, 1950; Jost, 1952). This led Curtis and Reynolds (1958) to suppose that the diffusion of radiogenic argon atoms occurs through associated-vacancy pairs of the type  $[\text{K}^+ | \text{Cl}^-]$  controlled by an activation energy of the order of 1 ev. The values obtained by us are twice as large. Therefore the Nernst-Einstein relation is not valid in the case of radiogenic argon diffusion, and its mechanism differs from that of self-diffusion of alkali ions.

To explore this situation, frequency characteristics of electrical conductivity for both samples of sylvites at different temperatures were measured by means of a  $Q$ -meter. The measuring device consisted of a co-axial condenser (FIGURE 13). A sieve fraction  $< 0.05$  mm. of the sample was poured into the space between the inner (1) and outer (2) electrodes. Parts 1, 2, and 4 were made of stainless steel and had low thermal conductivity. The insulation of the elec-

trodes was insured by means of two porcelain rings (3) cooled by running water to eliminate virtual changes of electrical insulation properties with temperature. Heating of the condenser was accomplished in a horizontal position by means of an electrical furnace to eliminate convection currents.

The  $Q = tg^{-1}\delta$  frequency characteristics were measured in the frequency range 50 kc. to 20 Mc. The active conductance was calculated from the formula:

$$g = b \, tg\delta, \quad (22)$$

where  $b$  is the reactance, and  $\delta$  the dielectric-loss angle.

Experimental curves for the red and rosy sylvites are given in FIGURE 14*a* and *b*. It may be seen that the heat activation factor affects chiefly the low- and middle-frequency ranges of the curves, while the high-frequency ranges merge to form a single string.

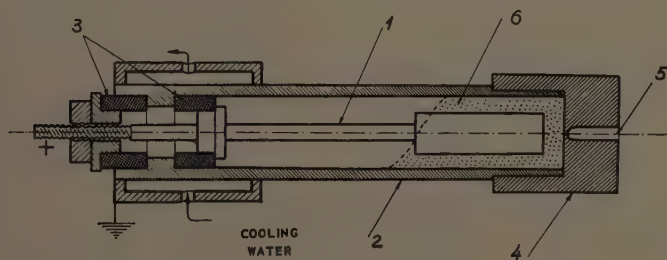


FIGURE 13. Condenser for conductivity and  $Q$  measurements.

The theory of dielectrics gives the following relation for the chief effective active current through a dielectric, having, in addition to transparent current losses, relaxation effects:

$$i_a = \left( g_1 + \frac{\omega^2 \theta^2}{1 + \omega^2 \theta^2} g' \right) U \quad (23)$$

Here  $g_1$  is the transparent conductivity and  $U$  the effective voltage of an angular frequency  $\omega$ , and  $\theta$  and  $g'$  constants depending on relaxation effects. In FIGURE 14*c* a set of theoretical curves calculated from Equation 23 is given with  $g_1/g'$  as a parameter. Comparing FIGURES 14*c* and *a* and *b*, we see that thermal activation seems also to affect only the  $g_1/g'$  ratio, that is, to change the transparent conductivity chiefly of sylvites.

To explore the nature of this conductivity, we placed the samples in a specially designed condenser and subjected them to high-intensity magnetic fields (up to 25,000 oersteds) and to  $K_\alpha$  X-ray irradiation of a copper anode (15 to 20 min.). In spite of a highly marked luminescence due to irradiation, no changes in conductivity at any frequencies in the range mentioned above were recorded. It seems therefore that the electrical conductivity is related to purely ionic rather than to electronic migrations.

The curves obtained by AC measurements do not allow determination of the activation energies of various conductivity processes  $\epsilon$  due to the disturbing

action of the second term of Equation 23. Therefore subsequent measurements could have been carried out with DC to obtain the transparent conductivity.

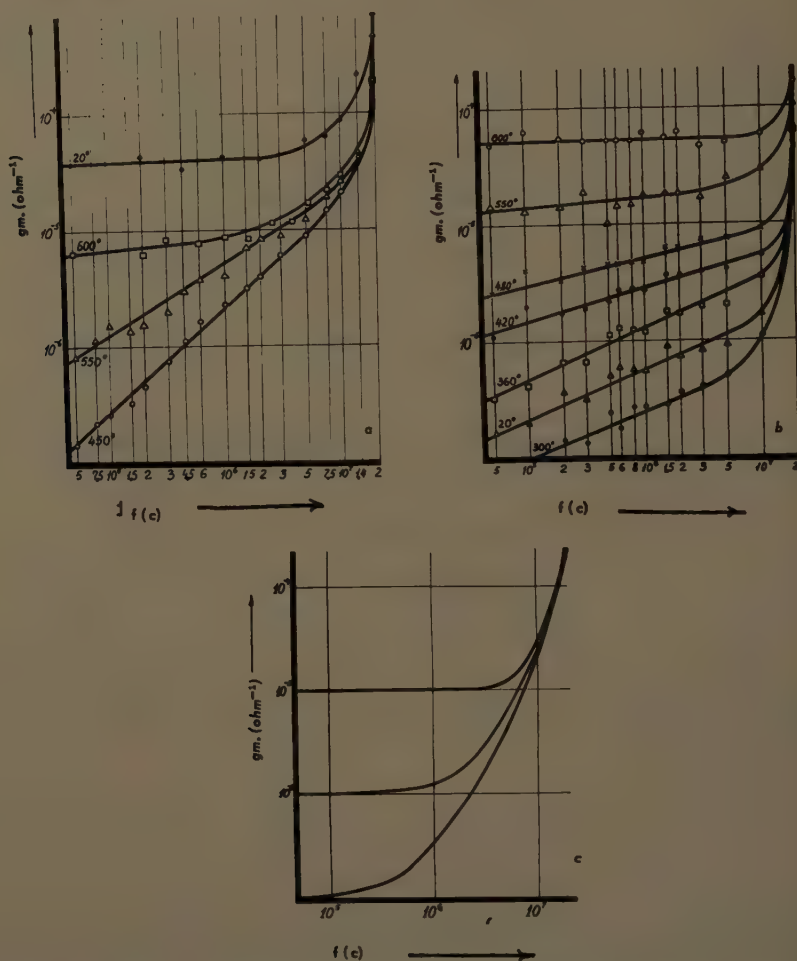


FIGURE 14a, b, and c. Frequency curves of electrical conductivity at different temperatures.

It is well known that the latter obeys the relation

$$\gamma = \gamma_0 \exp\left(-\frac{\epsilon}{RT}\right), \quad (24)$$

where  $\gamma$  is the specific conductivity. The results are given in FIGURES 15a and b.

It was shown by Mapother *et al.* (1950) that the ionic conductivity of alkali-halide crystals depends chiefly on the migration of positive ions through vacant lattice sites, due at low temperatures to bivalent impurities and at high temperatures to Schottky defects. Both of the measured curves (FIGURE 15) have

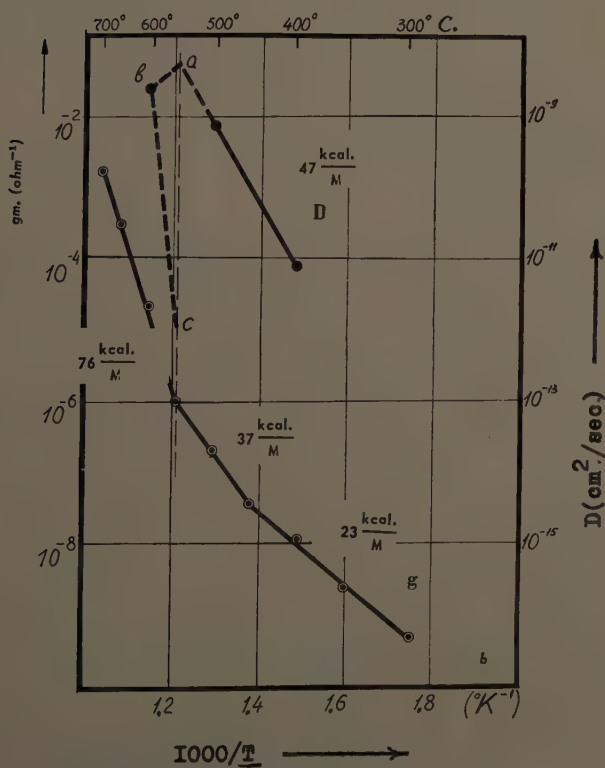
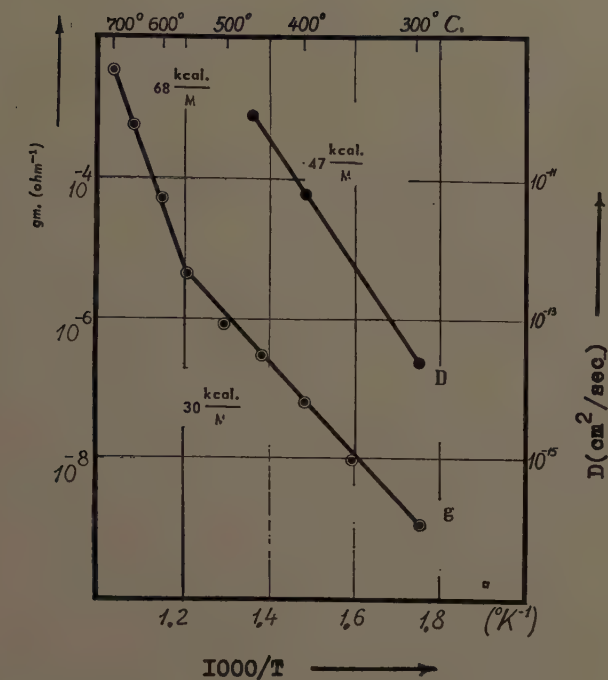


FIGURE 15a and b. Temperature dependence of  $D$  and  $g$  for sylvites.

a characteristic knee at  $550^{\circ}$  C. already mentioned by Mapother *et al.* (1950) as the boundary between the impurity conduction band and the region of conduction through Schottky defects. The curve for the rosy sylvite has an additional knee at  $480^{\circ}$  C. due probably to the more complicated structure of the impurity band. For comparison in the same FIGURE 15 the values of the diffusion constant are plotted. The values of activation energy are indicated at the corresponding parts of the curves.

It is seen that in the case of both the sylvites radiogenic argon diffusion takes place before the knee on the conductivity curve ( $550^{\circ}$  C.), that is in the impurity conduction band. The activation energy of diffusion in the impurity conduction band is much higher than the activation energy of conductivity both for the red and rosy sylvites. It seems that the additional knee on the conductivity curve of the rosy sylvite (FIGURE 15*b*) does not affect the radiogenic argon diffusion.

It has been mentioned that, in the temperature interval  $500^{\circ}$  to  $600^{\circ}$  C., the activation energy of diffusion rapidly decreases. This becomes readily explainable if we suppose that the activation energy of diffusion remains constant throughout the impurity conduction band (point *a* on curve in FIGURE 15*b*). There then occurs a discontinuity in the diffusion constant curve and the value of *D* falls rapidly to *c*, corresponding to argon leakage through normal Schottky defects. This value is expected to be rather low. Therefore it is supposed to be equal to the sensitivity threshold of the apparatus. Otherwise the activation energy in the interval  $550^{\circ}$  to  $600^{\circ}$  C. would be negative (*ab* in FIGURE 15*b*), which is impossible. Thus, the activation energy of argon diffusion is greater than the activation energy of conductivity not only in the impurity band but also in the region controlled by Schottky defects.

It follows, therefore, that the mechanism of radiogenic argon diffusion differs from that of ionic conductivity throughout the whole temperature interval investigated.

Curtis and Reynolds (1958) assumed that the diffusion of radiogenic argon in sylvite occurs through associated pair vacancies of the type  $\boxed{\text{K}^+ | \text{Cl}^-}$ . If we accept this assumption, the phenomenon of  $\text{K}^+$  ion diffusion appears to be quite different from that of argon atom diffusion. Wherever a  $\boxed{\text{K}^+}$  vacancy in a lattice is created, it is surrounded by occupied sites of  $\text{K}^+$ . Therefore the direct proximity of  $\boxed{\text{K}^+}$  and  $\text{K}^+$  is a fact. In the case of argon diffusion, however, we must consider the probability of proximity of  $\text{Ar}^{40}$  and  $\boxed{\text{K}^+ | \text{Cl}^-}$ . Therefore, the activation energy of radiogenic argon diffusion should be regarded as composed of three terms:

- (1)  $E_1$  accounts for the probability that the  $\text{Ar}^{40}$  atom makes a unit jump through a  $\boxed{\text{K}^+ | \text{Cl}^-}$  vacancy.
- (2)  $E_2$  accounts for the probability that the  $\boxed{\text{K}^+ | \text{Cl}^-}$  vacancy is created in one of the favorable positions, that is in the vicinity of  $\text{Ar}^{40}$ .
- (3)  $E_3$  accounts for the mobility of  $\boxed{\text{K}^+ | \text{Cl}^-}$  vacancies.

Therefore the  $\text{Ar}^{40}$  diffusion would be expressed as

$$D = D_0 \exp\left(-\frac{E_1 + E_2 + E_3}{RT}\right) \quad (25)$$



According to the estimates of Curtis and Reynolds (1958)  $E_1 \approx 1$  ev. The summary value of  $E$  that we obtained is  $\sim 2$  ev. therefore  $E_2 + E_3$  would be  $\sim 1$  ev.

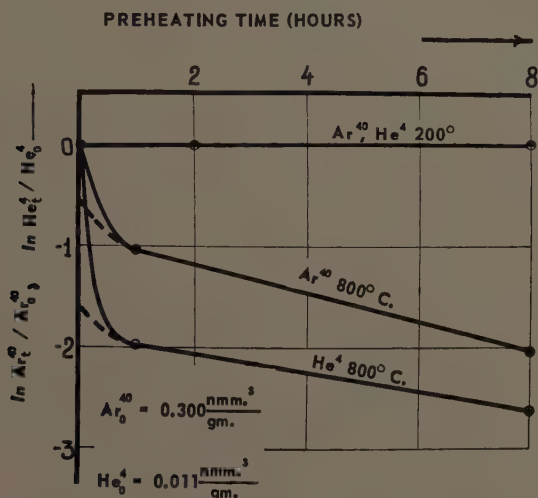


FIGURE 16.  $\text{Ar}^{40}$  and  $\text{He}^4$  leakage curves for a coal-like schist.

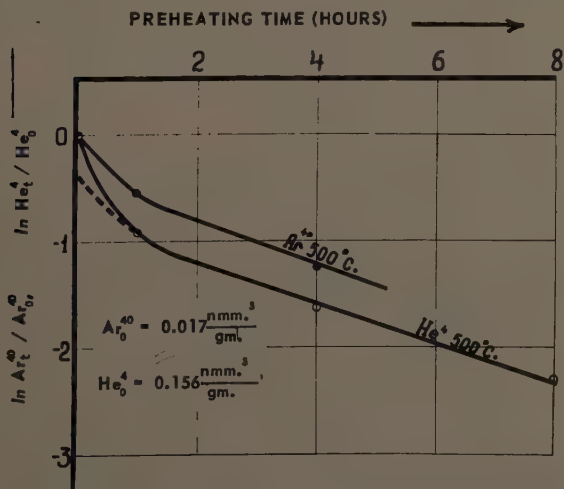


FIGURE 17.  $\text{Ar}^{40}$  and  $\text{He}^4$  leakage curves for a hornblende.

From this point of view, the discontinuity in the  $D$  curve in point  $a$  (FIGURE 15b) and the knee on the conductivity curve at this temperature could be explained as a result of dissociation of  $[\text{K}^+ | \text{Cl}^-]$  vacancies and the creation of Schottky defects.

Our experiments on simultaneous diffusion of helium and argon through some minerals seem to favor this explanation. In FIGURES 16, 17, and 18 the leakage

curves of argon and helium are given for a coal-like schist, hornblende and pyroxene, respectively. For all the samples a sieve fraction 0.1 to 0.2 mm. was used. On the same curves the initial argon and helium contents in  $\text{mm}^3/\text{gm}.$  are given. From the experimental curves the values of  $D$  were computed as above. In the case of pyroxene we obtained two sets of curves in order to compute the values of  $E$  and  $D_{300^\circ \text{K.}}$

The values of  $D_{800^\circ \text{C.}}$  obtained for the coal-like schist (FIGURE 16) are  $9.5 \times 10^{-11} \text{ cm}^2/\text{sec.}$  for  $\text{Ar}^{40}$  and  $5.5 \times 10^{-11} \text{ cm}^2/\text{sec.}$  for  $\text{He}^4$ . From FIGURE 16 we see that the computed curves (dotted lines) do not run through the origin of the coordinates but intersect with the ordinate axis, which seems to indicate some low-temperature losses. These losses are greater for helium and lower for argon. Although the coal-like schist is not a mineral but a rock, the fact

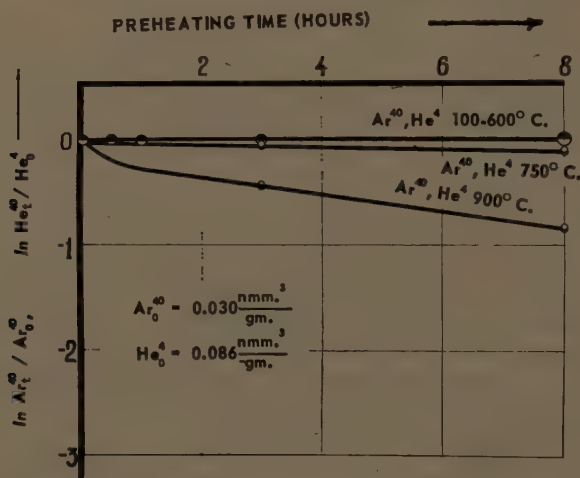


FIGURE 18.  $\text{Ar}^{40}$  and  $\text{He}^4$  leakage curves for a pyroxene.

of commensurability of the diffusion constants of  $\text{Ar}^{40}$  and  $\text{He}^4$  and the relation between the low-temperature losses is indeed rather instructive.

For the hornblende (FIGURE 17) the  $D_{800^\circ \text{C.}}$  values for argon and helium are equal and are  $1.5 \times 10^{-10} \text{ cm}^2/\text{sec.}$  For helium some low-temperature losses were observed, whereas for argon no losses were recorded.

In the case of pyroxene (FIGURE 18) the leakage both of helium and argon begins only at temperatures of the order of  $750^\circ \text{C.}$  The leakage curves for radiogenic argon and helium coincide within the limits of experimental errors at all preheating temperatures.  $D_{750^\circ \text{C.}} = 8.0 \times 10^{-13} \text{ cm}^2/\text{sec.}$ ,  $D_{900^\circ \text{C.}} = 8.0 \times 10^{-11} \text{ cm}^2/\text{sec.}$  No low temperature losses in this sample for either helium or argon are observed. From the  $Dt$  values the  $E$  and  $D_{300^\circ \text{K.}}$  were computed:  $E = 73,000 \text{ cal./mol.}$ ;  $D_{300^\circ \text{K.}} = 4.0 \times 10^{-50} \text{ cm}^2/\text{sec.}$

The fact that the diffusion constants of argon and helium in hornblende and pyroxene equal each other confirms the assumption that the diffusion of radiogenic gases is independent of their nature. Equal migration velocities of argon and helium atoms become explainable only when they move through vacant lattice sites.

Now we shall determine whether the obtained  $D$  values may cause radiogenic argon losses from minerals during geologic time. From FIGURE 4 we see that diffusion ceases to affect practically the radiogenic argon content at  $(Da^{-2}/\lambda) \leq 10^{-4}$ . This means that a value  $D = 10^{-27}$  cm.<sup>2</sup>/sec. does not cause any radiogenic argon losses in grain sizes  $>0.01$  mm. The  $D$  values obtained for all minerals studied are much less. Therefore it is obvious that radiogenic argon losses during geologic time cannot be related to diffusion and that we must look for other causes of these losses.

*On the mechanism of radiogenic argon loss by minerals.* Returning to the argon-leakage curves of phlogopite at 150 to 600° C. (FIGURE 5), we see that they have the form of horizontal straight lines. After a short transient time (usually after 0.5 hours preheating), the radiogenic argon content remains constant and is independent of further preheating time. The ordinates of these curves, however, decrease with increasing preheating temperature. These features of radiogenic argon loss resemble in a high degree the escape of an arbitrary gas in the course of desorption, obeying the same dependences and giving quite a similar picture.

In fact, Langmuir's sorption isotherm

$$\frac{V}{V_m} = \frac{bp}{1 + bp} \quad (26)$$

does not contain any time parameters and is a function of temperature only.

Here  $V/V_m$  is the relative quantity of the gas sorbed,  $p$  is the gas pressure, and  $b$  is a function of temperature of the form

$$b = \alpha \frac{\exp\left(\frac{q}{RT}\right)}{T^{1/2}}$$

( $\alpha$  is a numeric constant depending on the properties of the sorbent and sorbed gas and  $q$  is the heat of sorption).

We accept the relation 26 for further consideration. It is known that  $q$  usually equals several thousands calories per gm.-mole of gas sorbed. For estimation purposes, let  $q/R \approx 10^3$  and  $\alpha p = 10$ , obtaining reasonably good coincidence between experimental and computed data.

Hence the relation becomes finally:

$$\frac{Ar_m^{40}}{Ar_m^{40}} = \frac{10 \exp(10^3/T)}{T^{1/2} + 10 \exp(10^3/T)} \quad (27)$$

Here  $Ar_m^{40}$  denotes the amount of radiogenic argon in the first state in the phlogopite equal to 0.450 nmm.<sup>3</sup>/gm.,  $Ar^{40}$  being the amount of radiogenic argon retained in the first state at given preheating temperature.

In FIGURE 19 the empirical curve (full line) is plotted for comparison with the curve computed from Equation 27 (dotted line). The divergence between both the curves is rather small, which is a sufficient check of the fact that low-temperature losses in crushed micas are due to a desorption process.

Obviously the low-temperature losses in feldspar N65 at 400° C. (FIGURE 9) and rosy sylvite at 300° C. (FIGURE 12a) are due to the same process.

If, however, argon losses in minerals really occur as a result of desorption, the amount of these losses should be highly dependent on the specific surface of the mineral given. In this sense the glauconite, having a highly developed surface, warrants great interest.

It was shown by Gruner (1935) that, in glauconites, up to 25 per cent of the potassium is easily replaced by Tl by simply boiling it in a  $\text{TlNO}_3$  solution for

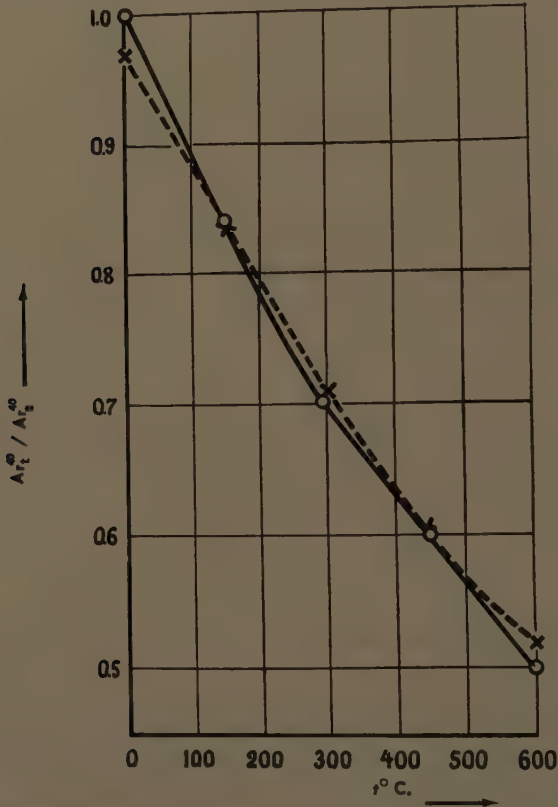


FIGURE 19.  $\text{Ar}^{40}$  leakage from phlogopite at low temperatures and the Langmuir isotherm.

several hours. He concludes that this part of potassium is located in the surfacial region of the mineral and is loosely bound to it.

Proceeding from these data, we suppose that a definite part of radiogenic argon, adequate to the surface potassium, must be expected to be very loosely bound to the glauconites. Therefore the amount of radiogenic argon in two samples of glauconite was determined as a function of preheating temperature, with the preheating time constant (8 hours for the first sample and 10 hours for the second). The data obtained demonstrate that the picture of argon leakage from both the samples is quite identical. The argon-leakage curve for one of the samples is given in FIGURE 20*b*. It may be seen that even at  $100^{\circ}\text{C}$ . about 20 to 25 per cent of the radiogenic argon escapes from the

mineral and that at 550° C. the whole of the argon is expelled. Hence we conclude that the radiogenic argon in glauconites, as in phlogopite, is distributed between two different states. The difference between these two cases is that argon leakage from these states in glauconite occurs in very narrow temperature bands. The first state of argon in glauconite, loosely bound to the crystal lattice, must therefore be attributed to the surface layer of the mineral.

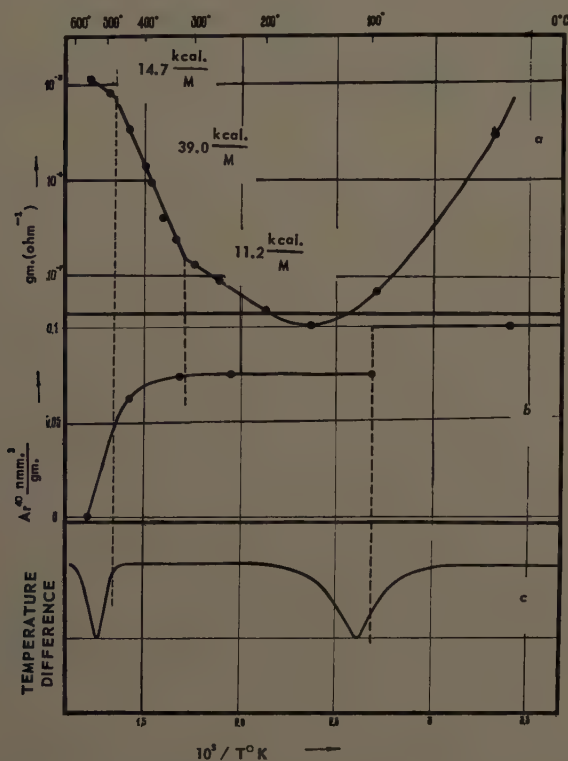


FIGURE 20a, b, and c.  $\text{Ar}^{40}$  leakage curves from glauconites compared with the temperature dependence of  $g$  and the thermogram.

The results of thermal analysis of glauconites lead to the same conclusions. The Kournakoff thermograms of glauconite (Tswietkoff and Valyashikhina, 1956) show two endothermic effects: between 100 to 200° C. and between 500 to 600° C. (FIGURE 20c). The first endothermic effect is due to the loss of the sorbed water, the second to the loss of constitutional water. The escape of radiogenic argon from glauconites coincides with these two thermal effects. It follows that the loss of sorbed water by glauconites causes the loss of radiogenic argon from the first state and that the loss of constitutional water leads to the loss of argon from the second state.

An experimental electrical DC conductivity curve for glauconite is given in FIGURE 20a, compared with the argon-leakage curve and thermograms. We see that the low temperature, decreasing part of the  $g$  curve coincides with the



loss of sorbed water and radiogenic argon from the first state. The decrease of the  $g$  curve is due to decreasing surface conductivity, confirming our assumption. At  $t \approx 350^\circ \text{C.}$  the  $g$  curve has the first knee, characterizing the beginning of argon escape from the second state. Finally, maximum rate of argon escape up to its complete loss is characterized by the second knee of the  $g$  curve at approximately  $480^\circ \text{C.}$  and an endothermic effect due to the loss of constitutional water. It is clear therefore that the leakage of radiogenic argon from glauconites is closely associated with the migration of sorbed and constitutional water and phase transitions of the first kind in them.

To explain the causes of radiogenic argon leakage from micas (phlogopite sample N250/53 and biotite sample N160/2798), we studied the conductivity

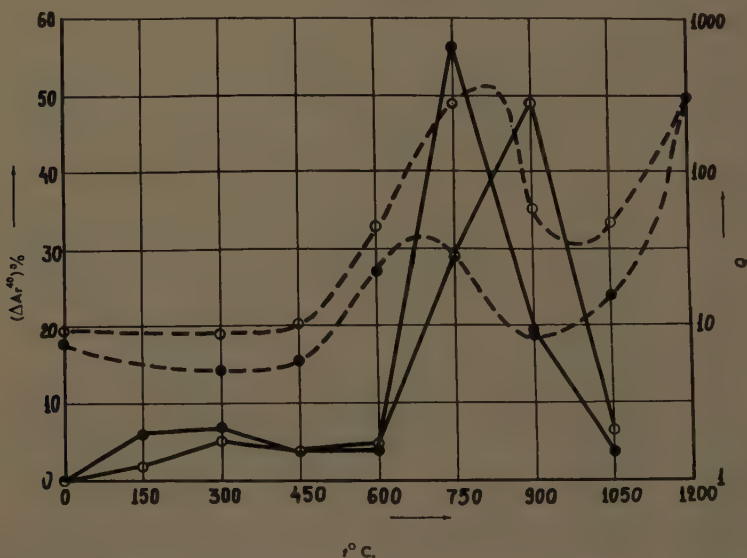


FIGURE 21.  $\text{Ar}^{40}$  losses, corresponding to temperature intervals  $150^\circ \text{C.}$ , compared with  $Q$  for phlogopite.

$g$  and the quality factor  $Q = tg^{-1}\delta$  for these samples. The quantity  $Q$  was chosen as a measure of virtually irreversible structural changes occurring in phlogopite and biotite during preheating.  $Q$  was measured in the frequency range 150 kc. to 12 Mc. by means of a  $Q$ -meter for micas previously preheated to various temperatures for 8 hours. All measurements were carried out at  $20^\circ \text{C.}$

FIGURES 21 and 22 show the temperature curves of  $Q$  (dotted lines) at a frequency 1.5 Mc. compared with argon losses in temperature intervals  $150^\circ$  ( $\Delta\text{Ar}^{40}$  per cent) for phlogopite and biotite respectively. ( $\text{Ar}_0^{40}$  for biotite =  $0.780 \text{ nmm.}^3/\text{gm.}$ ). The experimental points for the grain sizes 0.053 to 0.105 mm. are indicated by white circles, the points for sizes  $<0.053$  mm. by dark circles. It may be seen from FIGURE 21 that a maximum rate of argon loss at  $750^\circ$  and  $900^\circ \text{C.}$  for the phlogopite fractions  $<0.053$  and 0.053 to 0.105 mm. respectively correspond to maximum values of  $Q$  at temperatures  $600^\circ$  to  $750^\circ \text{C.}$

and 750° to 900° C. The picture for biotite fractions is quite analogous (FIGURE 22). Endothermic effects in phlogopite and biotite were observed in approximately the same temperature limits due to escape of constitutional water, these effects being displaced toward lower temperatures with decreasing grain size (Tswietkoff and Valyashikhina, 1956). Hence the maximum of  $Q$  appears to be a rather sensitive criterion of these effects. Thus the resemblance of glauconites and crushed micas becomes fairly complete.

FIGURE 23 shows temperature curves of DC conductivity ( $a$ ), for phlogopite ( $Ph$ ), and biotite ( $B$ ), compared with argon leakage after preheating the samples for 8 hours for grain sizes 1 to 3 mm. ( $b$ ). Both the micas have a single knee in the  $g$  curve correlating with the beginning of argon escape by means of

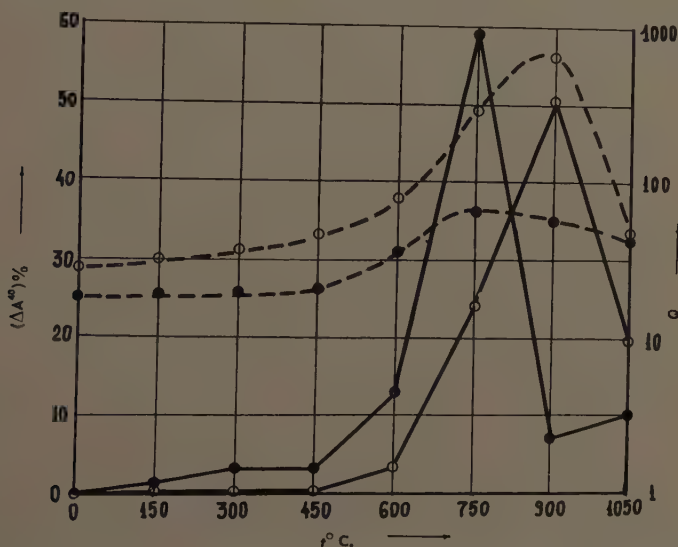


FIGURE 22.  $\text{Ar}^{40}$  losses, corresponding to temperature intervals 150° C., compared with  $Q$  for biotite.

diffusion. In finer fractions of micas, as mentioned above, there appear some desorptional losses of argon not characteristic for the processes in the bulk of the minerals and therefore not having any influence on the  $g$  curves. Comparing the activation energy of argon diffusion in phlogopite previously computed with the activation energies of conductivity, we find that the Nernst-Einstein relation again is not valid for micas, that is, in this case, the mechanism of  $\text{Ar}^{40}$  atom diffusion in micas differs from the mechanism of self-diffusion in the atoms.

It is well known that glauconite in its structural aspect is very similar to biotite (Gruner, 1935). FIGURE 24 shows for comparison the  $g$  curves for these two minerals. We see that the glauconite may be characterized by lower values of activation energies compared with biotite and also by the general displacement of the curves towards the low-temperature region. The second knee in the glauconite curve finds an analogue in biotite. In the case of bio-

tite, however, this knee may be located at more elevated temperatures ( $>1000^{\circ}\text{C.}$ ).

It follows from the above that the mechanism of argon escape from micas is very similar to that from glauconites. In both cases the argon escape is accompanied (or caused) by phase transitions of the first kind and by characteristic changes in the temperature curves of electrical conductance. The ele-

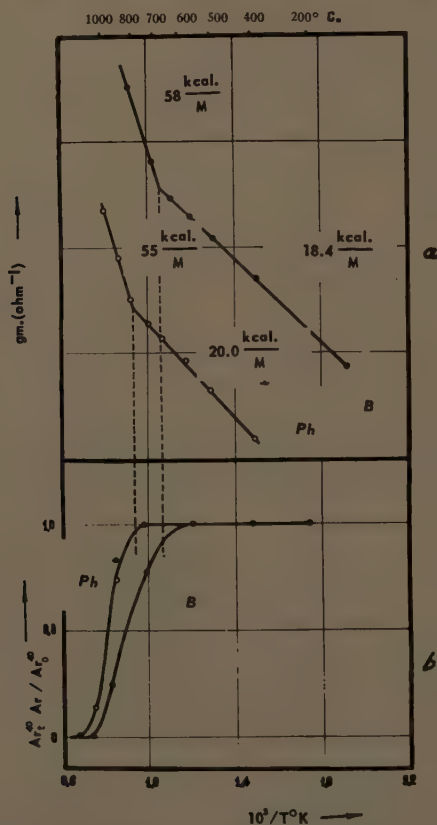


FIGURE 23a and b.  $\text{Ar}^{40}$  leakage curves for phlogopite and biotite compared with temperature dependence of  $g$ .

vated temperatures of all these effects in micas are explainable in terms of their higher cleavage.

Feldspars give the most complicated picture of argon leakage. The presence of different states of radiogenic argon or, as mentioned above, of different phases becomes explainable if it is supposed that feldspars are heterogenic systems, that at distinct temperatures phase-transitions occur in them, or that both these conditions take place simultaneously.

To detect phase transitions in feldspars, the  $Q$  parameter of the samples N35 and N65 preheated at various temperatures was measured when a month had passed after the heat treatment. It was discovered that dielectrical losses in

the samples remained constant within the limits of experimental error and were independent of temperature and duration of preheating. It was supposed however that virtual phase transitions in feldspars, taking place during short time intervals of heat treatment, might be reversible after some endurance. For this reason the DC conductivities and the specific heats  $C_p$  of both the samples at various temperatures were measured (grain size 0.053 to 0.105 mm.). The measurement of  $C_p$  of feldspars was carried out in an adiabatic-fused quartz

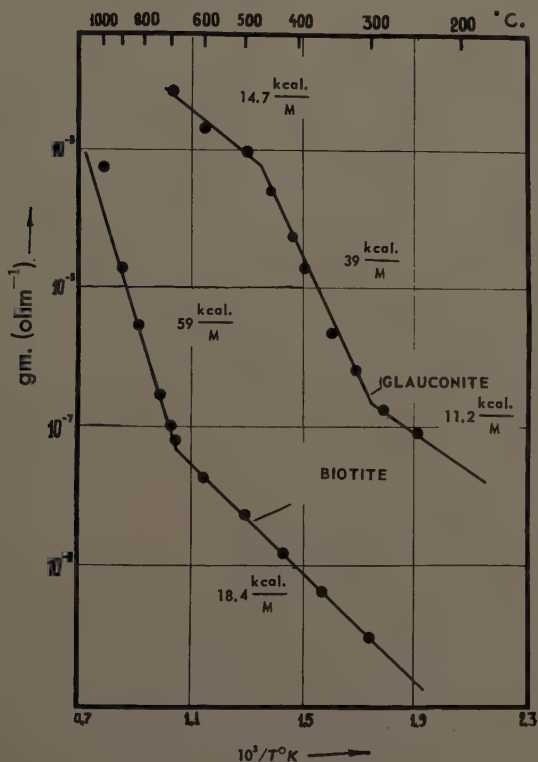


FIGURE 24. Temperature curves of  $g$  for biotite and glauconite.

calorimeter provided with evacuated cavities and heat screens to eliminate heat losses. The temperature of the sample was recorded by means of a thermocouple and an automatic potentiometer. The value of specific heat was computed graphically from the slope of the temperature records.

As the value of heating power was unknown although maintained rigorously constant, the specific heats are given in arbitrary units.

In FIGURES 25 and 26 the temperature curves of  $g$ ,  $C_p$ , and  $D$  for feldspar samples N35 and N65 respectively are given. Black circles denote the measured values of conductivity obtained with increasing temperature, whereas white circles refer to decreasing temperature. We see that the conductivity curves have two characteristic knees: the first at 550 to 600° C. and the second

at 680 to 700° C. As it was discovered that both samples were Or-Ab systems (N35 being K = 10.27 per cent, Na = 0.94 per cent; N65 being K = 9.84 per cent, Na = 2.82 per cent), pure samples of orthoclase and albite were measured separately to explain the twofold knees in the  $g$  curves (FIGURE 27).

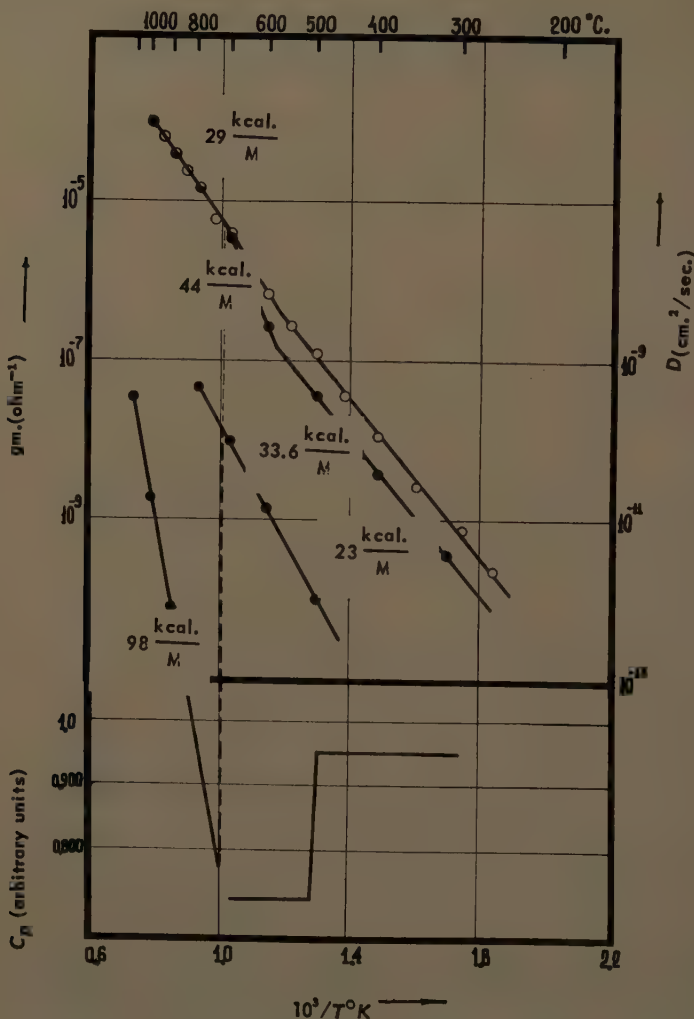


FIGURE 25. Temperature curves of  $g$ ,  $D$ , and  $C_p$  for feldspar N35.

Both the minerals just mentioned have a single knee in the  $g$  curve: the first at approximately 600° C. and the latter at 700 to 720° C. In FIGURE 27 we also plotted the  $g$  curve of feldspar N65 for comparison. Whereas the knee in the  $g$  curve of sylvite could be explained as a boundary of the impurity conduction band, in the cases of albite and orthoclase it is impossible, due to their complicated structures, to draw such a conclusion. It may be stated however



that lattice defects increase the mobility of interstitial particles. It may be supposed also that the feldspar sample contains a certain amount of heterogenic phase and that the two knees of the curves are due to "excessive" Ab and Or respectively (dotted lines in FIGURE 27). Both samples of feldspar were subjected to the action magnetic fields of high intensity and to X-ray irradiation, as in treating sylvites. As no changes in electrical conductivity could

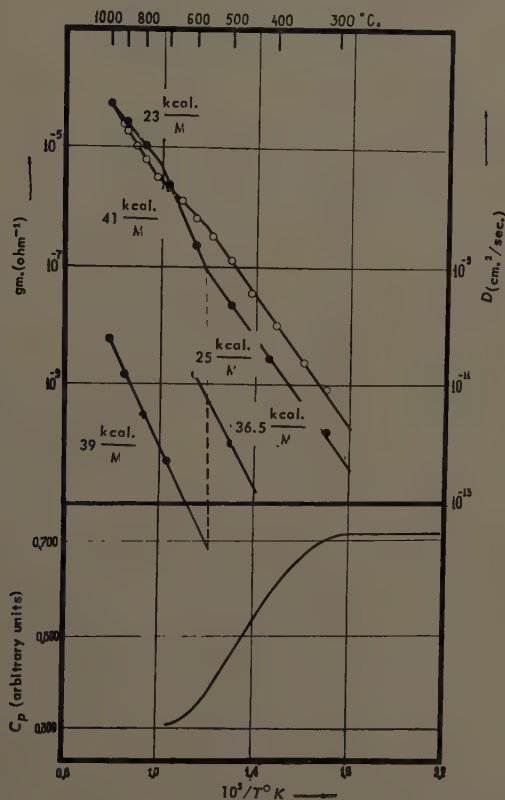


FIGURE 26. Temperature curves of  $g$ ,  $D$ , and  $C_p$  for feldspar N65.

be observed despite a very strong luminescence, we may conclude that the conductivity of feldspars is a purely ionic one.

To avoid negative values of activation energy of diffusion in the temperature intervals 800 to 900° C. for sample N35 and 600 to 700° C. for sample N65 (FIGURES 25 and 26 respectively) we suppose that, in the corresponding knee points of  $g$  curves, discontinuities of  $D$  occur accompanied by a jump in activation energy, as in the case of rosy sylvite. Such discontinuities are well known in the theory of alloys and physical chemistry (for example in the system  $\alpha\text{Fe} - \gamma\text{Fe}$ ).

In accordance with the above we must assume that the elevated values of  $D$  at 800° C. (N35) and at 600° C. (N65) are due to argon leakage from remain-

ing low-temperature phases. It must be noted that the discontinuity of  $D$  in sample N35 is related to the high-temperature knee of the  $g$  curve while, in the case of sample N65, it is related to the low-temperature knee. Possibly this difference is due to different positions of the feldspar samples on the phase diagram Or-Ab.

An attempt was made to clarify this difference by means of specific heat measurements. We see that, in the case of both samples, changes in the specific heat confirm a phase transition of the second kind. The beginning of

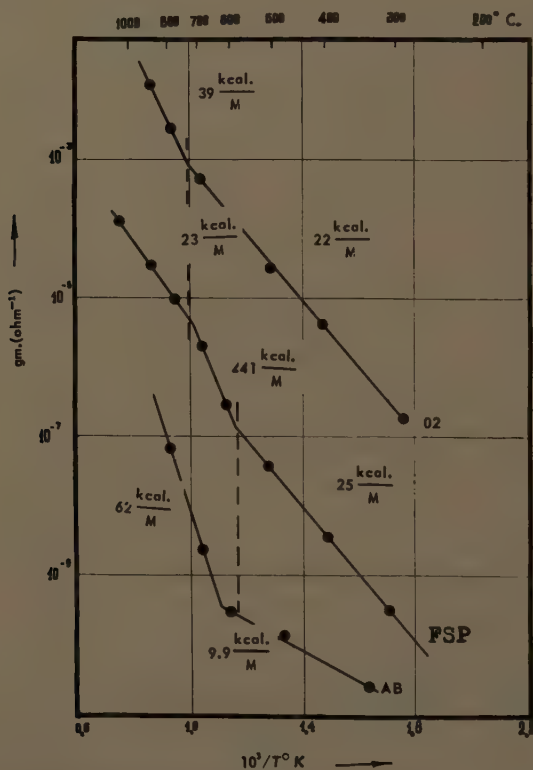


FIGURE 27. Temperature curves of  $g$  for albite, orthoclase, and feldspar.

perceptible diffusion in both feldspars coincides with the beginning of the  $C_p$  changes, which indicate the beginning of permutations in the crystal lattice as a whole.

Unfortunately, it was impossible for technical reasons to measure the  $C_p$  curves at temperatures higher than  $700^\circ\text{C}$ . in exploring the role of the upper knee in the  $g$  curve. Despite this fact, it may be seen that the jump in  $C_p$  in sample N35 is twice as small as that in sample N65. Hence the increase of entropy, a measure of irreversibility, in the case of sample N35 is also less as compared with sample N65. In fact, the divergence between the two branches of the  $g$  curves, corresponding to heating and to cooling, is much less in the case of sample N35.

The facts that the temperature characteristics of  $D$  for feldspars undergo some discontinuities in the points of nicks on the  $g$  curves and that the discontinuities are in a certain correlation with the entropy in the same temperature interval gives evidence that in the system Or-Ab at least one spinodal, bounded to the condition  $D = 0$ , takes place.

From FIGURES 25 and 26 it may be seen that the activation energy of argon diffusion differs from that of electrical conductivity, that is that the diffusion of radiogenic argon in feldspars also does not obey the Nernst-Einstein relation. In both cases the activation energy of argon diffusion is higher than that of self-diffusion. This fact shows that, as in the case of sylvite, the migration of  $\text{Ar}^{40}$  atoms in feldspars occurs through associated defects of the lattice and accompanies permutations of the latter. In the absence of lattice permutations, the migration of  $\text{Ar}^{40}$  atoms ceases. Similar to marked atoms (radioactive isotopes) used in biological research, radiogenic gases in mineral lattices are merely witnesses of more powerful processes: phase transitions occurring in geologic time.

To summarize the foregoing:

(1) The loss of radiogenic gases during geologic time by undisturbed minerals by means of volume diffusion is impossible.

(2) The loss of radiogenic gases occurs by desorption of these gases from boundaries created in the course of various secondary permutations in them.

(3) Migration of radiogenic gases in mineral lattices occurs through associated lattice defects accompanying phase transitions.

#### *On the Determination of True Absolute Age by the Argon Method*

As the radiogenic argon losses in geologic time occur by desorption from boundaries, the possible age discrepancy obviously will be determined only by the fraction of argon located at the surface layer of the mineral. Then a given mineral can be conventionally divided into two zones: a "steady" zone in which full preservation of radiogenic argon is warranted and an "unsteady" zone from which the escape of radiogenic argon is possible.

Following these considerations, fully reliable data as to absolute age may be obtained only from the  $\text{Ar}^{40}/\text{K}^{40}$  ratio of the steady zone, that is the potassium and radiogenic argon from the unsteady zone are to be removed.

It is known that feldspars frequently give underestimated age data. At the same time feldspars are the most widely occurring potassium minerals. Therefore the development of a technique that can obtain true argon ages is most reliable when applied to feldspars.

The removal of radiogenic argon from the unsteady zone of feldspars is carried out by means of a short low-temperature heat treatment (2 to 3 hours at 350 to 400° C.). For the extraction of potassium, however, a special technique was developed based on the exchange of potassium and thallium at elevated temperatures and pressures. Possibly this exchange is due to a secondary crystallization of the fraction of feldspar subjected to some secondary permutations.

The exchange reaction was carried out in a cylindrical bomb of stainless steel having low heat conductance (FIGURE 28). The diameter of the working space of the bomb was 10 mm. depth 200 mm. wall thickness 40 mm. Seal-

ing of the bomb was accomplished by means of a cone of soft steel. To avoid heating the screws and nuts a water cooling system was provided. To eliminate convection currents due to temperature differences of the upper and lower ends of the bomb, heating of the bomb was carried out in a horizontal position.

A weighted probe of feldspar (1 gm. grain size  $< 0.05$  mm.) was placed in the working space of the bomb and a certain amount of crystalline  $\text{TiNO}_3$  was added; this addition was necessary to obtain a saturated solution in the volume

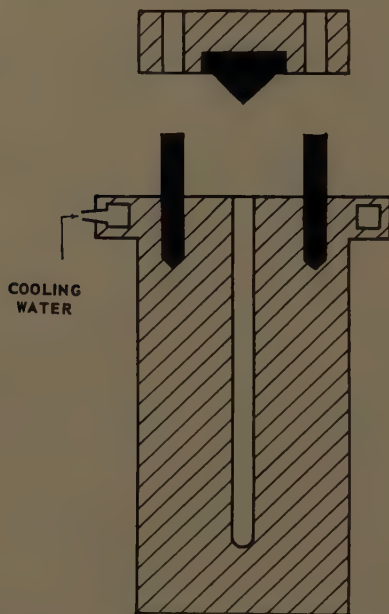


FIGURE 28. The potassium-extraction bomb.

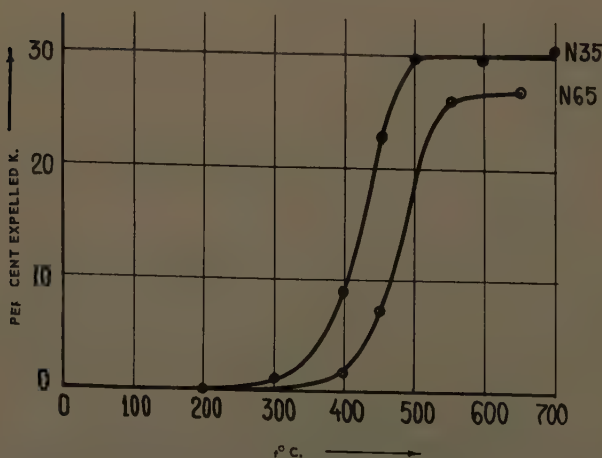


FIGURE 29. Potassium-extraction curves for feldspars N35 (dark circles) and N65 (white circles).

given. Finally the space was filled with distilled water and sealed. The bomb thus charged was heated to various temperatures for various lengths of time. Thereafter the potassium content in the solution and sample was determined by a chlor-platinate analytic procedure. In FIGURE 29 the curves of potassium extraction for feldspar samples N35 and N65 are given. It may be

TABLE 2  
DISTRIBUTION OF POTASSIUM AND ARGON BETWEEN STABLE AND UNSTABLE  
ZONES OF FELDSPARS

Sample	Bulk content		Unstable zone		Stable zone	
	Ar <sup>40</sup> nmm. <sup>3</sup> / gm.	K (%)	Ar <sup>40</sup> nmm. <sup>3</sup> / gm.	K (%)	Ar <sup>40</sup> nmm. <sup>3</sup> / gm.	K (%)
N35	0.962	10.27	—	3.03	0.962	7.18
N65	0.992	9.84	0.060	2.67	0.932	7.32
N1/1-5	0.670	8.60	0.030	1.64	0.640	6.86
N823/5	0.793	10.44	—	3.56	0.793	7.13
N6	0.036	5.50	—	1.85	0.036	3.51
N319	0.951	9.05	—	2.06	0.951	6.72

TABLE 3  
APPARENT AND TRUE AGE VALUES OF FELDSPARS AND MICAS

Sample	Age in m.y. ( $\times 10^6$ av.)	
	Bulk sample	Stable zone
Feldspar N35	1530	2000
Feldspar N65	1670	1950
Feldspar N1/1-5	1360	1575
Biotite N1/1-5		
Ar <sup>40</sup> = 0.525 nmm. <sup>3</sup> /gm.		1560
K = 5.81%		
Feldspar N823/5	1380	1860
Biotite N823/5		
Ar <sup>40</sup> = 0.620 nmm. <sup>3</sup> /gm.		1880
K = 5.18%		
Feldspar N6	160	275
Phlogopite N5		
Ar <sup>40</sup> = 0.088 nmm. <sup>3</sup> /gm.		285
K = 7.82%		
Feldspar N319	1720	2020
Phlogopite N250		
Ar <sup>40</sup> = 1.070 nmm. <sup>3</sup> /gm.		2010
K = 8.01%		

seen that the exchange of potassium to thallium proceeds to a certain limit and then remains constant despite subsequent increase of temperature (and pressure). This gives evidence that, in the circumstances given, only a definite fraction of potassium is capable of being replaced by thallium and this fraction is located in the unsteady zone.

For this reason the following working conditions were chosen: heating time, 4 hours, temperature, 600° C. Six samples of feldspars were investigated. The results of potassium and argon determinations are given in TABLE 2.



In TABLE 3 the values of absolute ages computed for bulk samples alone in the same manner as for the steady zone are given. In computing ages the following decay constants of  $K^{40}$  were used:  $\lambda = 5.3 \times 10^{-10} a^{-1}$ ,  $R = 0.118$ .

In order to check the reliability of ages obtained from the steady zone of feldspars, some age data were determined for micas: samples N1/1-5 and N823/5 on biotite fractions of equal age and samples N6 and N319 on phlogopite.

From TABLE 3 it may be seen that absolute age values obtained from the steady zone of feldspars fairly well coincide with ages of corresponding micas. The feldspars N35 and N65 give age values in full concordance with the lead method.

Therefore the techniques developed make it possible to obtain reliable argon-age values with feldspars and probably with other minerals and rocks in which the preservation of radiogenic argon is not warranted.

### Summary

A mass-spectrometric apparatus for quantitative extraction of radiogenic argon and helium from minerals has been described and an elementary theory of errors in quantitative argon determination developed. Time characteristics of argon escape from feldspars, micas, sylvites, glauconites and other minerals were discussed. Quantitative analysis shows two possible ways of argon loss from minerals: diffusion and desorption. Diffusion losses from minerals have been shown to be improbable, as the diffusion constant of most minerals at normal temperatures does not exceed  $10^{-30} \text{ cm}^2/\text{sec}$ . The most probable source of argon leakage is thought to be a desorption from boundaries created during phase transitions in geologic time. Processes of radiogenic argon migration have been shown to be closely associated with electrical conductivity and specific heat  $C_p$ , although the Nernst-Einstein relation seems not to be valid. Finally a special technique was described that is thought to give true argon age values coinciding with those obtained by the lead method.

### Acknowledgments

We are grateful to D. I. Scherbakoff and to G. D. Afanasieff of the Academy of Sciences of the U.S.S.R. for their encouragement during the course of the work performed and to J. L. Kulp of the Lamont Geological Observatory, Columbia University, Palisades, N. Y. for his kind invitation to us to contribute this article.

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## SUMMARY OF DISCUSSION OF DISCORDANT ZIRCON AGES

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Experiments with different fluxes and spiking procedures on zircons with discordant ages have shown that the lead concentrations are accurate within 1 per cent. The discordant ages are therefore caused by natural phenomena and are not due to faulty analytical procedures.

A study of the systematics of discordant ages for seven zircons from the Blue Ridge province of western North Carolina and eastern Tennessee shows that the discordances could have been produced by alterations of U/Pb ratios that took place in the Paleozoic era about 350 million years (m.y.) ago. The same age has been measured for pegmatites and for micas from several metamorphic rocks in the area. It is concluded from this that the discordant zircon ages can be related to metamorphism attending the formation of the Appalachians. A problem is created by the fact that the discordant zircons are from an area of low metamorphic grade, while zircons from the Piedmont Province in Maryland and Pennsylvania, where the metamorphic grade is high, have given nearly concordant ages. Although the discordances seem to be related to the mountain-building processes, they are not a direct function of the intensity of metamorphism as recognized by the geologist.

Discordant zircon ages found in northern Michigan and Finland display such regularities that episodic loss of lead does not seem to be indicated. The discordances are taken to indicate that, under even the most favorable geological conditions, zircon loses 5 to 10 per cent of its lead per billion years.

S. C. ROBINSON (*Geological Survey of Canada, Ottawa, Canada*): Does your diffusion theory work as well for metamict as for nonmetamict zircons?

TILTON: The model would work. I am not certain whether there are any metamict zircons in the things plotted. On the 1100 m.y. chord there are zircons that are very metamict and some that are almost nonmetamict. The lead would vary from, for example, 35 ppm in the Pikes Peak sample to about 400 ppm in some of the Ontario zircons. Therefore this theory does not seem to be a function of the degree of metamictization.

B. J. GILETTI (*University of Oxford, Oxford, England*): May I ask why the same situation is found for such different minerals as uraninite, zircon, and thucolite?

TILTON: Some of the monazites are an exception. Monazites that have U-Pb ages greater than Pb-Pb ages must be omitted. Aside from this omission, it is possible to explain this agreement. All that is required is that the  $D/a^2$  be different between a monazite and a uraninite by some constant amount and that they simply evolve through a natural sequence of events. As regards the thucolites, Olavi Kouvo has stated (personal communication) that many of the thucolites in Finland are actually small particles of uraninite in an organic matrix; therefore, although they are called thucolites (the actual translation from the Russian was the word carburane, which I assume is thucolite, but this may be uraninite again), I think it is just a matter of different  $D/a^2$  from one

mineral to another, depending more on the particular circumstance than on the mineral and monazites mixed with uraninites.

H. D. HOLLAND (*Princeton University, Princeton, N.J.*): Given the  $D/a^2$  values that you have on your lines, what would be found if the zircons were to be heated in the laboratory? Would there be appreciable diffusion in measurable times?

TILTON: I do not know but I think there would not be. This value can be calculated, but I have not attempted it. It works out in geologic time for a  $D/a^2$  of 10. The lead on the average moves quite a small distance, a fraction of the radius. I do not know whether this could be calculated.

HOLLAND: May I ask if L. O. Nicolaysen has any data on this?

G. J. WASSERBURG (*California Institute of Technology, Pasadena, Calif.*): The  $D$  will not be significant in laboratory times unless it is heated until it becomes very large.

HOLLAND: Of course, but may I ask what happens after  $1400^\circ \text{C}$ ?

WASSERBURG: This question cannot be answered unless the activation energy, which cannot be told from this curve, is known.

J. L. KULP (*Lamont Geological Observatory, Columbia University, Palisades, N.Y.*): In many cases, as has been shown, the 207–206 ages in the discordant zircons seem to be close to the correct age. However in other cases, of course, it is low. If I follow your model correctly, the correct 207–206 age might be obtained whether bulk radiogenic lead was leached continuously over the history of the mineral or leached just recently, for example by some sort of ground-water activity. However to obtain the low age, would it not be necessary to change the grain size or at least the internal surface area during the history of this model?

TILTON: No, if I understand your question.  $\text{Pb}^{207}$  is generated earlier than  $\text{Pb}^{206}$  in this mineral because of the shorter half life of  $\text{U}^{235}$ ; therefore proportionately more  $\text{Pb}^{207}$  than  $\text{Pb}^{206}$  is lost; that is why the line does not go to the origin. As regards the actual time of loss of the lead that could be leached, lead that had been loosened over the entire life of the mineral, it would not be relevant whether it was carried away yesterday or the instant it was made.

L. O. NICOLAYSEN (*Bernard Price Institute of Geophysical Research, University of the Witwatersrand, Milner Park, Johannesburg, Union of South Africa*): In 1956 I discussed various tests that could be applied to the diffusion mechanism. A test with a different radii of zircons or some similar radioactive mineral from the same rock provided the best test. I still feel that this is the case for the following reason. As you may have noticed, in the case where we started from 1900 m.y., the curve is almost a straight line over most of the path.

In the case of minerals such as monazites and uraninites, our experience has been that recent alterations, zero-time alterations due to the leaching effect of ground water, are important, and this would be a process giving a straight line joint between 1.9 and the zero point.

However this inverse square dependence on radius in the case of zircons provides a very clear test for the mechanism, and I think we still should strive toward that particular goal.

WASSERBURG: Tilton has given a very beautiful explanation of this phenom-

enon. In his discussion he followed other workers in relating diffusion flux to gradients in chemical potential. This is a minor matter, but the problem, which in fact was solved, is the solution to the diffusion equation with a source for a particular boundary condition. The calculations were made subject to the assumption that the flux is proportional to the gradient of the concentration. It is assumed only that the equation and boundary conditions adequately describe the physical situation. No relationship with the chemical potentials is assumed. To state this problem in these terms is undesirable since it obscures the phenomenological formulation of the problem and what was actually done.

NICOLAYSEN: I totally disagree on this point. I believe that this process is effective in the case of the uraninites that are minute, that is,  $\frac{1}{10}$  to  $\frac{1}{20}$  mm. in diameter, that are small, circular, oval spheres, and that in many cases are surrounded by halos of a galena. There is a continuing diffusion of lead from the uraninite into the galena so that, from the standpoint of the concentration gradient, the work is against the concentration but, in terms of free energy, there is a very large sink.

WASSERBURG: That is indeed correct. Ultimately it is the second law of thermodynamics that governs the direction of a reaction. However the detailed relationship of the kinetics of the process to the thermodynamic functions is a completely different matter. The kinetic equation cannot be derived in general from the thermodynamic equations. The diffusion equation is used because experimental evidence supports it.

HOLLAND: May I ask if it is not a matter of whether the diffusion rate is in fact proportional to the mass gradient or to the gradient of the chemical potential and whether this is not a physical problem?

WASSERBURG: In attempting to describe the effects of chemical stability and the direction of the process, appropriate boundary conditions are used. In cases such as that described by L. O. Nicolaysen, the situation is even more complicated because of a chemical reaction.

Indeed, in the simple case of two phases of variable content (at constant T), the *direction* of matter transport for a species is from high to low concentration. This information hardly suffices to determine the explicit form of the diffusion equation or, in particular, that a "diffusion constant" exists.

HOLLAND: As I understand it, G. R. Tilton thinks the better assumption is that the rate of diffusion is proportional to the chemical potential gradient, followed by the assumption that this is proportional to the concentration.

TILTON: That the activity coefficient is 1 is the assumption that is often made, for example in dilute solutions.

WASSERBURG: All that is assumed is that Fick's law is the governing law for diffusion; it is not relevant whether it has anything to do with anything else.



## URANIUM-LEAD METHOD ON ZIRCONS\*

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Sarah Deutsch

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In this paper I report some data obtained by a study of zircons from a single block of granite approximately 1.5 cu. ft. in volume.

The purpose of this investigation was to better our understanding of geological, mineralogical, and physical-chemical controls on the behavior of U-Pb equilibria in these systems. Along with such parameters as zircon grain size, zoning, and morphology, my associates and I hoped to couple the study with a fair understanding of the geologic history of this particular granitic mass; this understanding is based upon a five-year field-mapping and laboratory-investigation of the area in which the mass is found.

The chemical procedures we have employed in this work have been derived in part from the work of G. R. Tilton, of the Carnegie Institution of Washington, Washington, D.C. It is largely due to Tilton's work and that of Claire Patterson of the California Institute of Technology, Pasadena, Calif., that we have techniques for working with small quantities of uranium and lead in such a way that contamination problems, particularly contamination by common lead, can be minimized.

The samples under consideration were derived from a single petrographically homogeneous block of Johnny Lyon granodiorite, a Pre-Cambrian igneous mass in Cochise County, Ariz. This granodiorite has an abundance of zircons that, like those of many granites, tend to be liberated in their original grain size and shape during appropriate crushing procedures. It was possible to obtain large quantities of zircon sized by their prism diameters. Size fractions of zircons studied are shown in TABLE 1.

The grain morphology of the various size fractions was sufficiently constant to give average length to width ratios of 2.3 to 2.5 for all four fractions. Moreover, 60 to 70 per cent of each fraction consisted of unbroken grains and about 30 per cent had only one broken termination. The remaining small percentage consisted almost entirely of prismatic barrels minus terminations.

In performing the concentration of the zircons, it was possible to obtain readily samples more than 99 per cent pure. The impurities, however, were dominated by one phase, a completely metamict uranothorite. This is, as indicated in the  $\alpha$ -particle autoradiograph in FIGURE 1, a highly radioactive phase. Indeed, the very small amount of uranothorite contributed more  $\alpha$ -particle activity to the concentrate than did the zircon. Clearly, at this stage it was necessary to recognize that for our purposes this was not an assemblage of pure zircon but rather a uranothorite-zircon assemblage.

It was necessary to devise a chemical technique for preferentially dissolving the uranothorite out of the concentrates and, by careful comparison with hand-

\* Publications of the Division of the Geological Sciences, California Institute of Technology, Pasadena, Calif., Contribution No. 1012.

picked concentrates, we satisfied ourselves that the solvent in no way attacked the zircon. The solutions or washes containing the uranothorite were subsequently analyzed isotopically.

In TABLE 2 are data for uranium and radiogenic lead concentrations and apparent ages in the various zircon size fractions.

It is quite clear that there is a systematic change in the uranium and associated radiogenic leads as a function of size. Isotopic analysis of the leads show

TABLE 1  
SIZE FRACTIONS OF ZIRCONS

Screen size	Prism diameter
Retained 200 mesh	75-150 $\mu$
Retained 300 mesh	54-75 $\mu$
Retained 400 mesh	37-54 $\mu$
Passed 400 mesh	20-37 $\mu$



FIGURE 1.

from  $\text{Pb}^{206}/\text{Pb}^{208}$  ratios that even more significant variations in the thorium to uranium occur and are also apparently size dependent.

In FIGURE 2 a "concordia" plot of  $\text{Pb}^{206}/\text{U}^{238}$  versus  $\text{Pb}^{207}/\text{U}^{235}$  is shown for the four size fractions of zircon and for two different samples of uranothorite washes.

The analytical errors are of the size represented by each point symbol on the graph. The line generated by these points intersects the concordia plot at about 90 and 1660 million years (m.y.).

Very briefly I shall summarize some additional experiments performed in

taking zircons apart by a sort of communal stripping procedure. First, almost all of the zircons in this granodiorite are visibly zoned with internal morphological habits approximately similar to the external euhedrons. We have developed a technique for stripping the outer layers from sized aggregates of these zircons. In this way it is possible to determine isotopic data for the different layers and the core of a "composite" zircon of that size. It is possible to treat these parts as individual radioactive systems, and we have found that the several parts of a stripped 200-mesh size fraction also fall, with about the

TABLE 2  
URANIUM AND RADIOGENIC LEAD CONCENTRATIONS WITH APPARENT AGES IN  
ZIRCON SIZE FRACTIONS

Size fraction	U (ppm)	Pb <sup>rad</sup> (ppm)	Pb <sup>208</sup> /Pb <sup>206</sup>	Apparent ages (m.y.)		
				Pb <sup>206</sup> /U <sup>238</sup>	Pb <sup>207</sup> /U <sup>235</sup>	Pb <sup>207</sup> /Pb <sup>206</sup>
R 200 mesh	510 ± 5	100.3 ± 0.5	0.182	1070 ± 20	1270 ± 20	1630 ± 20
R 300 mesh	542 ± 5	103.1 ± 0.5	0.191	1030 ± 20	1230 ± 20	1610 ± 20
R 400 mesh	569 ± 5	103.1 ± 0.5	0.196	980 ± 20	1200 ± 20	1620 ± 20
P 400 mesh	579 ± 5	106.7 ± 0.5	0.201	995 ± 20	1205 ± 20	1610 ± 20

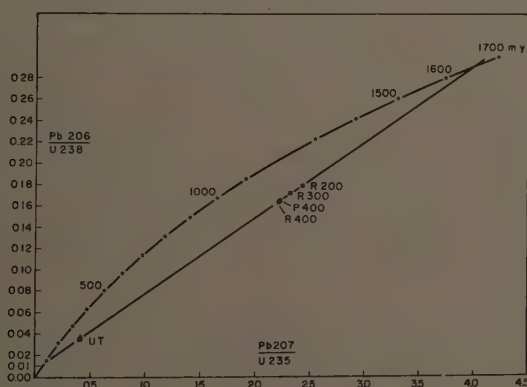


FIGURE 2. Concordia plot of four zircon size fractions and two acid washes of uranorthorite.

same precision as the previous data, on the line or chord shown in FIGURE 2. The various parts of the composite zircon therefore may be considered to be independent radioactive systems that have shared in the history of the granodiorite, as have the various zircon size fractions and the uranorthorite.

At this point it is worthwhile to review several important points:

(1) A zircon concentrate is rarely (at least in our experience with many granites) a homogeneous suite, either in terms of uranium concentration or U/Th ratio.

(2) The zircons may show significant variations in these parameters as a function of size and zoning.

(3) Zircon concentrates may have impurities that although minor in amount, may contribute significantly to the radioactivity of the assemblage.

(4) Although zircons may be indeed highly discordant, many apparent discordant relations reported in zircons may be the result of admixtures of zircon and minute quantities of phases even more susceptible to disturbance of their radioactivity equilibrium than the zircon. Perhaps some of G. R. Tilton's acid-washing data may be explained this way.

With these points in mind, let us return to the significance of a concordia plot such as the one shown in FIGURE 2. Those U-Pb systems in which the apparent ages based upon  $Pb^{206}/U^{238}$ ,  $Pb^{207}/U^{235}$ , and  $Pb^{207}/Pb^{206}$  ratios are in exact agreement will be represented by points on the smooth concordia curve. This is assuming of course that such problems as knowledge of decay constants, analytical procedures, and corrections for common lead can be controlled as G. W. Wetherill has pointed out elsewhere in this monograph. Even when we do appear to have these problems in hand we still commonly find U-Pb systems in which these apparent ages are not in agreement. In such cases the systems are represented by points that fall off the concordia curve and are considered discordant. Wetherill has shown lucidly that it may be possible to evaluate a discordant system in order to recognize a simple two-episode history for the radioactive system: (1) origin and (2) a single subsequent disturbance prior to the present time.

Clearly all of the systems reported in this study, all of which have been separated from a single "concentrate" of zircon, are discordant. It is further clear that it is possible to explain the line they generate on the concordance plot as reflecting a simple two-episode history originating about 1660 m.y. ago and profoundly disturbed approximately 90 m.y. ago. Each of the systems apparently responded to the disturbance to a degree dependent upon such physical and chemical factors as size, composition, and location within the crystals. The complex of systems appears to provide more profound possibilities than just an "age" for the rock. It gives an insight into the subsequent history and suggests lines of investigation for stabilities of radioactive systems that may become important indicators for conditions of metamorphism.

How well does this postulated history agree with field observations? That the Johnny Lyon granodiorite was originally formed in Pre-Cambrian time can be clearly demonstrated. It supports, under a classical Eparchean unconformity, the younger Pre-Cambrian Apache group and an overlying Paleozoic section containing middle Cambrian fossils near its base. The granodiorite and the entire section, including younger beds assigned to the Bisbee group of early Cretaceous age, have been profoundly deformed and injected by dikes and veins related to the so-called Laramide orogeny. In this region the orogeny is accompanied by major plutonism that can be placed as occurring sometime after the Lower Cretaceous section was deposited. A younger age limit on this plutonism may be lower Miocene, although the relations are not quite satisfactory. No major deformational and plutonic episodes are known here in the interval between the emplacement of the Johnny Lyon granodiorite and the Laramide orogeny. It would appear therefore that the ages derived from the two-episode interpretation of the concordia plot are compatible with a well-defined regional geologic history.



G. R. Tilton has suggested elsewhere in this publication an interpretation of continuous lead loss to explain concordia plots of data apparently similar to the data shown here. I cannot evaluate quickly this alternative.

However there is something of great interest in the episodic explanation. That there are areas where episodes might occur and indeed do occur cannot be denied. These can be seen from field geologic criteria.

There is material of value to be obtained from the kind of approach we have attempted, that is, in studying a *family* of U-Pb (and thorium of course) systems. Even if the kind of situation suggested does prevail and there is continuous loss, it should be indicated by the data to be seen in assemblages. Perhaps, however, it does not follow the simple explanation offered. For example, it did not appear that Tilton's points plotted too well with respect to assignable analytical errors. Nevertheless, the general nature of the phenomenon must be accepted.

The question is whether information is to be obtained from looking at assemblages of U-Pb systems in a given rock? This question does not refer to a single number from each of a half dozen different rocks subject to all the problems of correlation that are concerned whenever a granite is said to be a certain age or equivalent to that granite. This concerns systems that are fundamentally related to each other by common location (for example, in the same outcrop) and by petrology and that are accepted as subject to common history. The fact that it is not said that all these mineral phases reflect precisely the same common history is an important point. If a number of these different phases in a single system are considered, whether these phases are defined by grain size, by mineral composition, or otherwise, and if it is found that they show systematic relationships in their deviations from equilibria, there is a clue to something far more important than the two intersections of these curves: a clue to an important reflection of the petrogenetic processes.

When we finally have some idea of what constitutes thresholds for the disturbances in each of these systems, the K-Ar, the Rb-Sr, and these various U-Pb systems in different hosts, we shall have something constituting just as valuable criteria for geological conditions as those other parameters that we now use, such as solid solution and polymorphism.

#### *Discussion of the Paper*

G. R. TILTON (*Carnegie Institution of Washington, Washington, D.C.*): I disagree with the paper to the extent that I do not think, considering the rather stringent assumptions necessary and the fact that we are dealing with several continents, that all those zircons were exactly the same ages. The 2.8 line serves as a guide to the range that might be expected, while the samples can be placed between a 2.8 and 2.6 wedge.

Also, I probably left the impression, in my discussion elsewhere in this monograph, that I think this allowance takes care of all discordant zircon ages; that was an oversight on my part. In southern Appalachia, in North Carolina, and in Tennessee there is a sequence of zircons that definitely does not fit the  $D/a^2$  sequence. They are about 450 to 1150 m.y., and this does not satisfy the  $D/a^2$ . Perhaps this Arizona sequence is another such example.



## THE AGE OF THE TARAKSKY GRANITE MASSIF AND OTHER FORMATIONS OF THE YENISEY RIDGE

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In studying the geologic structure of Pre-Cambrian formations we encounter a number of difficulties that are primarily connected with the necessity of classifying strongly metamorphosed rocks according to age. These difficulties are aggravated by the fact that metasomatic processes, superimposed at a later date, mask the original interrelationships and create the appearance of a genetically single process. Consequently the methods of absolute geochronology assume special importance for the classification of Pre-Cambrian structures and for diagnosis and dating of superimposed processes. Work carried out in recent years provides a long list of interesting examples of the changes and corrections these methods introduce into previous geologic concepts of various regions of the Pre-Cambrian.

The Yenisey Ridge is one of the elements of the folded framework of the Siberian Platform. The study of its rather complex geologic history is also of considerable importance for our understanding of the geology of the eastern Sayan Mountains and the basement of the western margin of the Siberian Platform adjacent to the ridge and the eastern part of the West Siberian Depression.

According to Yu. A. Kuznetsov,<sup>1,2</sup> we can distinguish in the southern part of the Yenisey Ridge the Lower Archean Kan and Upper Archean Yenisey metamorphic complexes, the granitization of which was connected with the Taraksky and Posol'nensky gneiss granites. In addition to these, a number of Proterozoic schists penetrated by intrusions have been identified.

In recent years a different viewpoint has been encountered among some geologists, according to which "the gneisses and schists of the metamorphic complexes, as well as the granite bodies of the Angara-Kan portion of the ridge, are regarded as a single complex that has arisen as a result of potassium metasomatism of basic rocks."<sup>3</sup> In this view, Archean formations within the ridge can be differentiated only on a conditional basis. The actual age of the Taraksky granites is not Archean but considerably more recent and perhaps even Cambrian. These conclusions have been based on the following arguments:<sup>3</sup> (1) determinations of the absolute age of Taraksky granites, based on the total lead content of monazite, yielded an age of 500 m.y.; (2) xenoliths of carbonate composition containing algal remains have been demonstrated in the Taraksky granites; and (3) in the area of the Kurysh River the influence of Taraksky granites on rocks of the Lower Cambrian can be seen.

Special expeditions and field observations made by us in 1958 and 1959 showed the conclusion that xenoliths of carbonate rocks are present in the granites of the northern part of the Taraksky massif is incorrect. A direct influence of these granites on the Cambrian (if they are Cambrian) quartzite sandstones cannot be proved so simply since this influence (contact) is not

established directly, and the presence of inclusions in quartzite sandstones may also be explained as being of a sedimentary origin. In any case, and even if the inclusions are of a metasomatic character, this still is not an argument in favor of a recent age for the granites, as will be evident from the data to be presented below. From the same data it will also be apparent that a determination of age on the basis of total lead content may lead to serious errors.

In the present paper we set forth the results of age and isotope determinations, including several values that have already been reported.<sup>4,5</sup> Our methods of selecting and analyzing the material have for the most part been described earlier.<sup>4,5</sup> By way of supplementing the previous report, we might add that potassium was determined by the picrate method. The isotopic composition of lead was determined on the MS-2 mass spectrometer: macroquantities of lead in the form of lead iodide and microquantities (from a few tenths of 1  $\mu\text{g.}$  to 100  $\mu\text{g.}$ ) in mixtures of copper iodide and lead iodide. All ages based on lead ratios have been recalculated on the basis of special tables published recently.<sup>6</sup> A number of inaccuracies in the reports published earlier<sup>4,5</sup> have thus been corrected. The age according to the argon method was calculated on the basis of the following constants:

$$\lambda_k = 5.5 \times 10^{-11} \text{ year}^{-1}$$

$$\lambda_\beta = 4.72 \times 10^{-10} \text{ year}^{-1}$$

$$\frac{K^{40}}{K^{41} + K^{39}} = 1.22 \times 10^{-4}$$

The results of our determinations are summarized in TABLES 1, 2, and 3. TABLE 1 presents age determinations on two monazites from different sections of the Taraksky massif (or the migmatite field connected with it). The position of **N**, taken from gneiss granite inclining toward the field of the Lower Kan granite massif, is somewhat uncertain. However the presence of accessory monazite, which is totally uncharacteristic of this massif, in this gneiss granite gives us reason to consider the rock in this sample as genetically related to the Taraksky massif. The table also includes the results of determinations for zircon from pegmatite of the Tatarsky alkaline massif and for orthite from pegmatite of the Ayakhta granite massif (the portion of the ridge beyond the Angara).

The uranium content of the monazites analyzed was rather constantly within the range of 0.2 to 0.3 per cent, except for **1** (0.7 per cent) and **2, 9**, and **10**. The low content in the last two can be explained as a secondary phenomenon (see below). In monazite, **9** to **13**, the  $\text{Pb}^{204}$  content was markedly elevated.

These samples also display the greatest age spread, which indicates a more intense alteration of the minerals. For monazite **4**, which was altered more than **3**, from the same rock, the  $\text{Pb}^{204}$  content is much greater; for **4** the age spread is also greater. This indicates that the  $\text{Pb}^{204}$  admixture (that is, non-radiogenic lead) is the result of the addition of lead during alteration of the mineral and not of trapping at the time of crystallization. For this reason, a correction for nonradiogenic lead is introduced for these monazites that is based on the lead composition of the more recent galena (TABLE 2, **6**). For

TABLE 1  
RESULTS OF DATING OF MINERALS BY THE LEAD METHOD

No.	Rock sample	Mineral	Site	Content (%)				Content of lead isotopes (%)				Age (m.y.) based on ratios:				Brief description
				U	Th	Pb		Pb <sup>304</sup>	Pb <sup>306</sup>	Pb <sup>307</sup>	Pb <sup>308</sup>	Pb <sup>307</sup> / Pb <sup>306</sup>	Pb <sup>307</sup> / U <sup>238</sup>	Pb <sup>308</sup> / U <sup>238</sup>	Pb <sup>208</sup> / U <sup>232</sup>	
1	Zh	Monazite	Kan River, right bank, area of Komarov dam	0.70	6.36	0.77		0.014	26.99	3.18	69.81	1845	1880	1905	1845	Granitoid vein portion of migmatite
2	E	Monazite	Kan River, 4.5 km. below mouth of Kurysh River, right bank	0.12	4.71	0.42		0.025	8.23	1.15	90.60	1610	1660	1805	1745	Porphyroblastic granite
3	D	Yellow monazite	Taraka River, river bed; 1 km. above Tayezhny	0.27	6.36	0.54		0.013	12.69	1.56	85.74	1795	1725	1650	1590	Alluvium
4	Brown	Brown monazite	Taraka River, river bed; 1 km. above Tayezhny	0.21	5.94	0.42		0.032	11.07	1.61	87.29	1760	1560	1426	1346	Alluvium
5	D	Monazite	Taraka River, river bed; 1 km. above Tayezhny, but from bed-rock of the left bank	0.30	5.78	0.49		0.094	16.57	2.93	80.42	1795	1680	1640	1450	Porphyroblastic granite
6	V	Monazite	Kurysh River, left bank, 800 km. from mouth	0.22	5.61	0.42		0.076	13.22	2.44	84.26	1745	1605	1525	1350	Migmatite-granite
7	K	Monazite	Kan River, right bank, 3 km. above mouth of Potanchet River	0.22	5.85	0.47		0.02	13.24	1.87	84.67	2005	1870	1815	1484	Migmatized cor-dierite-garnet-biotite gneisses
8	I	Monazite	Kan River, right bank, 2.5 km. below mouth of Kazachya River	0.26	8.39	0.58		0.03	11.71	1.64	86.62	1735	1670	1660	1308	Migmatized cor-dierite-garnet-biotite gneisses
9	G	Monazite	Kurysh River, left bank, 900 km. from mouth	0.10	4.54	0.18		0.13	14.76	3.01	82.10	1260	1400	1505	690	Migmatite-granite
10	B	Monazite	Kurysh River, left bank, 1100 km. from mouth	0.048	4.96	0.15		0.218	13.81	4.21	81.76	1368	1740	2015	502	Pegmatoid rock from lenticular formation in contact zone
11	N	Monazite	Kan River, right bank, 1 km. below Kuzhet Island	0.27	7.58	0.21		0.20	12.06	3.61	84.13	798	530	479	481	Gneiss-granite
12	Ayakhta	Orthite	Great Pit River, 15 km. south-east of Pit-Gorodok	0.057	0.028	0.014		0.15	35.69	4.96	59.20	1270	665	514	602	Pegmatite
												1220	735	586	604	
13	Tatarka	Zircon	Tatarka River, midpoint	0.08	0.32	0.016		0.30	42.45	6.40	50.85	1050	640	540	445	Pegmatite

TABLE 2  
ISOTOPIC COMPOSITION OF LEAD FROM VARIOUS FORMATIONS

No.	Site	Isotopic composition				Remarks
		Pb <sup>206</sup> / Pb <sup>204</sup>	Pb <sup>207</sup> / Pb <sup>204</sup>	Pb <sup>208</sup> / Pb <sup>204</sup>	Pb <sup>207</sup> / Pb <sup>206</sup>	
1	Ore outcrop on Angara River	16.0	14.42	33.90	0.901	First stage of mineralization, galena
2	Ore outcrop on Angara River	16.34	14.84	34.04	0.908	Second stage of mineralization, galena
3	Ore outcrop in area of Great Pit River	17.31	15.96	36.65	0.922	Galena
4	Bogunay gold ore deposit	16.26	15.20	36.78	0.935	Galena
5	Granite D, Taraksky massif	16.32	15.31	36.79	0.938	From microcline phenocrysts
6	Granite D, Taraksky massif	17.33	15.37	36.92	0.887	Accessory galena
7	Migmatite K	17.39	15.33	36.82	0.885	Accessory galena
8	Gneiss—granite A	17.67	15.29	36.78	0.865	Accessory galena
9	Granite A	20.37	15.39	36.89	0.756	Accessory galena
10	Pegmatite B, Taraksky massif	17.69	15.40	37.85	0.870	Lead from microcline
11	Kan pegmatite deposit	17.92	15.54	38.0	0.868	From microcline of vein "Giant"
12	Kiya alkali massif	18.41	15.30	36.78	0.831	Galena from streaks in biotitized contact rock
13	Tatarsky alkali massif	19.05	16.07	39.35	0.84	Galena from pegmatite

TABLE 3  
RESULTS OF DATING BY THE ARGON METHOD

No.	Site	Sample	A 10 <sup>-6</sup> cm. <sup>2</sup> / gm.	K content (%)			Age (m.y.)
				Flame photometer	Chemical	Mean	
1	Sample A	Biotite	18.3	6.02	5.73	5.88	696
2	Sample A	Rock	10.4	3.9			582
3	Sample E	Biotite	19.7	7.44	7.48	7.46	592
4	Sample E	Rock	5.0	2.94	3.13	3.03	415
5	Sample K	Biotite	40.2	7.0	7.43	7.22	1100
6	Sample I	Biotite	48.6		6.88		1311
7	Kiya massif, contact	Biotite	11.7		6.91		412
8	Kan pegmatite deposit	Muscovite	11.7		8.55		334
9	Tatarsky granite massif						
	Sample I	Biotite	21.0		6.45		716
10	Bogunay gold deposit: gneisses from core sample	Golden biotite	9.2		6.72		334



the orthite **12**, a correction is also introduced on the basis of the composition of recent lead (TABLE 2, **11** and **13**). For the zircon sample a correction is made on the basis of galena lead from the same deposit (TABLE 2, **13**).

The ages thus obtained for these monazites may be placed in the following groups:

(1) This group contains ages that are the same for all four isotope ratios, represented by only one monazite (**1**). This monazite is the basis for judging the actual age of the others. For **2**, reduced ages are obtained on the basis of the ratios  $Pb^{207}/Pb^{206}$  and  $Pb^{207}/U^{235}$ . This is most likely related to some error in the determination of  $Pb^{204}$  content; when the amount of  $Pb^{207}$  present is small, errors in the determination of  $Pb^{204}$  have a very marked effect on the corrected value for  $Pb^{207}$ . The similarity between the ages based on  $Pb^{206}/U^{238}$  and  $Pb^{208}/U^{232}$  argues in favor of this idea.

(2) These are ages giving a characteristic picture (**3** to **8**), in which the  $Pb^{207}/Pb^{206}$  age  $>$   $Pb^{207}/U^{235}$  age  $>$   $Pb^{206}/U^{238}$  age  $>$   $Pb^{208}/U^{232}$  age, with the age based on the first of these ratios practically coinciding with the age of monazite **1**.

For monazite **7**, the age based on  $Pb^{207}/Pb^{206}$  is somewhat greater than that of **1**.

Ages based on the ratio  $Pb^{207}/U^{235}$  vary within the range 1870 to 1560 m.y.;  $Pb^{206}/U^{238}$  ages vary between 1815 and 1426 m.y., and  $Pb^{208}/U^{232}$  ages vary between 1590 and 1308 m.y. For this last ratio, the age scatter is the smallest and, if we exclude **3**, it is within the range 1308 to 1484 m.y. for the other five. In general, there is a greater difference between the  $Pb^{206}/U^{238}$  age and the  $Pb^{208}/U^{232}$  age than between the ages based on the ratios  $Pb^{207}/U^{235}$  and  $Pb^{206}/U^{238}$ .

(3) This group includes monazites yielding the lowest  $Pb^{208}/U^{232}$  ages, between 481 and 690 m.y. The ages based on the other ratios are very diverse, but in all cases the  $Pb^{207}/Pb^{206}$  age is much more recent than it is for monazites of the first two groups. It should be emphasized that for monazites of the third group the nonradiogenic lead correction in the value for  $Pb^{207}$  is large, being more than two to six times the actual amount of radiogenic  $Pb^{207}$ ; for this reason, values calculated on the basis of  $Pb^{207}$  are much less accurate than those for monazites in the other two groups. For **9** and **10** the  $Pb^{207}/U^{235}$  and  $Pb^{206}/U^{238}$  ages are greater than the age based on  $Pb^{207}/Pb^{206}$ , and the age based on  $Pb^{206}/U^{238}$  is greater than the  $Pb^{207}/U^{235}$  age. For **10** the difference between the  $Pb^{206}/U^{238}$  age and the  $Pb^{207}/U^{235}$  age is greater than it is for **9**, and for the same sample (**10**) the uranium content is lower than for any other.

If we take the actual age of the monazites to be the mean of all the ages for the monazite in the first group, that is, the value  $1870 \pm 100$  m.y., all the other ages are explained if we assume that lead has been removed from the minerals, accompanied in some instances by the removal of uranium. The most complete removal of lead has occurred in the case of **11**. For this monazite the age based on  $Pb^{207}/Pb^{206}$  is the most recent and is the closest to the other three ages for the same specimen, which almost coincide. We can therefore take a figure around 400 m.y. as the date of the process of lead removal. It follows that, as we suggested,<sup>4</sup> the minimum age based on  $Pb^{208}/U^{232}$  can in general be taken as the earliest possible time for the superimposed process. If there is a



series of such determinations with similar  $\text{Pb}^{208}/\text{U}^{232}$  ages, the minimum age may, to a fairly good approximation, date the time of removal. This approximation will become better as the corresponding  $\text{Pb}^{207}\text{-Pb}^{208}$  age becomes relatively more recent and closer to the  $\text{Pb}^{208}\text{-U}^{232}$  age.

For 9 and 10 the removal of uranium exceeded the removal of lead. The removal of a considerable quantity of uranium explains its present low concentration.

The quantitative relations of the ages obtained for orthite\* and zircon follow the general pattern. On the basis of this fact, the actual age of orthite and zircon could scarcely be less than 1500 m.y. Nevertheless further determinations are necessary for these samples since the determination of the ratio  $\text{Pb}^{207}/\text{Pb}^{206}$  is not sufficiently accurate. It is interesting that the  $\text{Pb}^{208}\text{-U}^{232}$  ages are the same for these minerals as for the monazites in the third group: that is, the superimposed process is dated at the same moment in time for the trans-Angara section as for the southern part of the ridge.

Lead was also removed from the monazites in the second group; in most cases this was accompanied by a partially compensating removal of uranium. This is shown by the fact that the difference between the  $\text{Pb}^{206}\text{-U}^{238}$  age and the  $\text{Pb}^{208}\text{-U}^{232}$  age is generally greater than the difference between the  $\text{Pb}^{206}\text{-U}^{238}$  age and the  $\text{Pb}^{207}\text{-U}^{235}$  age. From a specially calculated nomogram<sup>7</sup> it is seen that, if even a few tenths of 1 per cent of the lead is removed, or as much as 90 per cent, the discrepancy between the  $\text{Pb}^{206}\text{-U}^{238}$  age and the  $\text{Pb}^{208}\text{-U}^{232}$  age will be less than 100 m.y. For minerals of more recent age this discrepancy will be smaller, and for young minerals it will be inconsequential. The small differences between the  $\text{Pb}^{208}\text{-U}^{232}$  ages of the five monazites in the second group and the almost complete absence from this group of  $\text{Pb}^{208}\text{-U}^{232}$  ages falling between the actual age of the minerals (that is, about 1850 m.y.) and the  $\text{Pb}^{208}\text{-U}^{232}$  age characteristic of the third group of monazites may serve as a basis for the conclusion that the  $\text{Pb}^{208}\text{-U}^{232}$  age of monazites in the second group indicates still another stage of lead removal, at a time around 1300 m.y., but not earlier.

The fact that it is not permissible to determine age from total lead content has already been mentioned in our previous papers,<sup>4,5</sup> Additional data cited in this paper again make it completely obvious that determinations of age on the basis of total lead content without isotopic analyses may result in large errors.

Thus, from everything we have said, it follows that for the entire series of monazites studied we obtain an age close to the true age from the ratio  $\text{Pb}^{207}\text{-Pb}^{206}$ ; from the ratio  $\text{Pb}^{208}\text{-U}^{232}$  we obtain the greatest reduction in age; from the relation between ages based on the various isotope ratios, superimposed processes not only can be demonstrated but can also be dated.

Particular cases may be exceptions to this rule, for example, where the removal of uranium exceeds the removal of lead, as in the case of monazites 9 and 10. However these are easily established. Moreover, cases in which uranium has been added or in which there has been selective removal of one of the lead isotopes will naturally be exceptions. Nevertheless the low figure for the  $\text{Pb}^{208}\text{-U}^{232}$  age cannot be related to selective removal of  $\text{Pb}^{208}$ . In the

\* As is evident from TABLE 1, age calculations with corrections based on two different lead samples yield similar results.

process of removal of considerable quantities of the lead accumulated in the mineral, accompanied by intensive alterations in the mineral, mixing of all the isotopes must inevitably take place. In this case selective removal is not very probable. It is possible if there is removal of small amounts (a few per cent) not accompanied by noticeable alteration of the mineral, as occurs in experiments on leaching.

From the quantitative relationships between the ages it is evident that, under those geochemical conditions in which a considerable removal of lead and uranium occurs in our case, thorium is relatively inert. This does not exclude the possibility that a small amount of thorium may be removed simultaneously; this is all the more probable in view of the fact that thorium geochemistry has demonstrated the mobility of thorium under hydrothermal conditions in a long list of instances. However in our case the removal of thorium can scarcely result in a significant increase in the  $\text{Pb}^{208}\text{-U}^{232}$  age.

TABLE 2 shows isotopic compositions of lead from various formations. Of these, three are for lead samples taken from microclines (**5**, **10**, and **11**), four are for accessory galenas (**6** to **9**), and the rest for galenas of various deposits and ore outcrops.

According to the data of N. P. Yermakov (personal communication) two generations of galenas can be distinguished in the ore outcrops on the Angara River. Analysis No. 1 is for a first-generation galena; No. 2 is for a second-generation galena. They are similar in so far as regards lead isotope composition and yet they are somewhat different. Their composition is unusual; they are characterized by disproportionately large amounts of  $\text{Pb}^{206}$  in relation to  $\text{Pb}^{207}$  (and  $\text{Pb}^{208}$ ), considering the small amounts of  $\text{Pb}^{207}$  and  $\text{Pb}^{208}$  present, which points to lead of a rather old age. The age of the lead can be estimated approximately by comparing  $\text{Pb}^{207}/\text{Pb}^{204}$  and  $\text{Pb}^{208}/\text{Pb}^{204}$  with the corresponding ratios for quite accurately dated lead. Thus the age of the lead deposited in the first stage of mineralization can be estimated at 1500 to 2000 m.y. The question of the age of the ore itself is debatable. Two main ideas can be considered in the factors determining the age of the ore outcrop:

(1) The lead in the ore outcrop is genetically connected with a process of ancient metamorphism of even earlier rocks, disturbing the Th/U ratio. The age of the lead agrees with the age of the ore outcrop and dates the time of metamorphism.

(2) The lead is an ancient lead (for example, from limestones) redeposited as a result of a comparatively recent process, the age of which remains uncertain. The former interpretation is more probable.

Lead in the galena of the Pit ore outcrop (**3**) is more recent in composition than the first two and the two after it (**4** and **5**) and is also anomalous. However it is anomalous in a different way: it is relatively rich in  $\text{Pb}^{207}$ . Leads **4** and **5** are genetically entirely different: the first is from a galena of a gold-ore deposit, and the second is taken from microcline of porphyroblasts of the Tarasky granites. The fact that their compositions are identical indicates that their ages are similar: of the order of 1000 m.y. or somewhat more.\* The

\* We do not believe it is possible to calculate the age of lead ore and other leads accurately on the basis of their isotope composition, although this is rather commonly done. This question will be discussed elsewhere.

appearance of microcline porphyroblasts in the Taraksky granites is thus a superimposed process of a much later date. It is possible that the age of the phenocrysts may be less than 1000 m.y. if the composition of the lead in the phenocrysts reflects the results of removal of the primary lead from the rock (aged 1850 m.y. or more) and of the recent lead (much less than 1000 m.y.). This interpretation is less probable.

To the next group of lead samples—those from accessory galenas (**6** to **9**, TABLE 2)—we may also add, on the basis of its composition, lead of galena from the Kiya alkali massif (**12**). It is noteworthy that this group is characterized by the same  $Pb^{208}/Pb^{204}$  and  $Pb^{207}/Pb^{204}$  ratios as the two previous samples (**4** and **5**). This probably means that they are genetically rather close. The anomalous composition of the lead in **9** is explained by the elevated uranium content in the granite of this sample, while the thorium content is normal ( $U = 19 \times 10^{-4}$  per cent;  $Th = 1.9 \times 10^{-3}$  per cent;  $Th/U = 1$ ). For this granite sample a large part of the uranium is apparently not connected with accessory zircon or accessory monazite. It is interesting to note that for a single sample (**D**) the lead compositions of a porphyroblast (**5**) and a galena (**6**) are different: they differ markedly with respect to  $Pb^{206}/Pb^{204}$ , which is considerably greater for the galena lead; it follows that the latter is of more recent age. It is difficult to draw a definite conclusion as to the age of these galenas. In all probability the lead of these galenas was not added to the rocks by later hydrothermal solutions, but was borrowed from the rock itself, reflecting the make-up of the lead connected with potassium metasomatism (the formation of porphyroblasts).

This idea is strengthened by the similarity of these samples with respect to  $Pb^{208}/Pb^{204}$ . If it is correct, the age of all the accessory galenas may be quite recent, may correspond to the time of appearance of the most recent metasomatic processes and to the formation of pegmatites (that is, about 400 m.y.). If the similarity of the compositions of these leads with respect to  $Pb^{208}/Pb^{204}$  (and also  $Pb^{207}/Pb^{204}$ ) is real, the same considerations will probably hold for the lead of the Kiya galena as well. We call attention to the similarity between the  $Pb^{208}-Pb^{204}$  value for the Pit ore outcrop and the  $Pb^{208}/Pb^{204}$  values for all the lead samples of which we have been speaking. The assumptions that have been made about the age of the accessory galenas are supported by the age based on the ratio  $Pb^{208}/U^{232}$  for the monazite of sample **N** (481 m.y.), which is the richest in accessory sulfides, particularly galena. The leads taken from microcline of a lenticular pegmatite formation from the eastern contact zone of the Taraksky massif (**B**) and microcline of the "Giant" vein of the Kan pegmatite deposit are similar to each other in composition and are clearly different from all the others. Their age is about 400 m.y., as indicated by the age of muscovite from the Kan deposit (see TABLE 3) and the  $Pb^{208}-U^{232}$  age for monazite of **B** (TABLE 1, **10**).

The last analysis (**13**) points to an anomalous composition for the lead of galena from the pegmatite of the Tatarsky massif. Its age also is probably close to 400 m.y., since the  $Pb^{208}-U^{232}$  age for zircon of the same massif is 445 m.y.

Age determinations by the argon method for the Taraksky granites and mig-

matites, as well as for Kan pegmatite deposits and golden mica from the Bogunay deposit (TABLE 3), give values in the range 400 to 1300 m.y. Here also, two groups may be distinguished: 330 to 700 m.y. and 1100 to 1300 m.y. As yet we have not succeeded in recording higher values corresponding to about 1850 m.y. All these data indicate the existence of at least two successive deposition processes. We may note that for **K** and **I** the  $\text{Pb}^{208}\text{-U}^{232}$  age is close to the age based on the argon method; and the argon-method age of pegmatites of the Kan deposit is in complete agreement with the age based on the lead composition of microcline from this deposit. For **E** the age based on argon is much more recent than the age based on  $\text{Pb}^{208}/\text{U}^{232}$ . For **A** it is greater than the probable age of the last process of alteration, that is, about 400 m.y. The age of golden mica (TABLE 3, 10) from pyroxene gneisses of the Bogunayev deposit is 330 m.y. A similar mica developed in pyroxenes in the contact zone of certain veins in the Kan deposit. The formation of this type of mica was consequently connected with a late metasomatic process.

The figure 716 m.y., obtained for the age of biotite from the Tatarsky granite massif, should be regarded as the minimum possible age of the granites. This figure apparently dates the time of metasomatic alteration of granites of this massif.

It follows from these data that within the Yenisey ridge there has occurred a whole series of processes of change of more ancient rocks and secondary formation of younger rocks, together with ore deposition processes, in the range of 1850 to 330 m.y.

The Taraksky massif is an example of an ancient massif formed in three main stages: the first, 1850 m.y. ago, apparently corresponds to the first period of granitization of rocks of the Kan complex; the second, in the interval 1000 to 1300 m.y., corresponds to an intense potassium metasomatism; the third, about 400 m.y. ago, corresponds to a hydrothermal and probably to some extent potassium-metasomatic transformation of granites accompanied by pegmatite formation. Further study should make this preliminary scheme more accurate and more complete. Of primary importance is the fact that the superimposed processes can be diagnosed and dated by an analysis of age data based on individual isotope ratios and on a comparison of these data with the results of isotope analysis of lead from ore outcrops and microclines, as well as by determinations of age by the argon method. It is evident that possible utilization of the strontium method would help greatly in deciphering the existing interrelationships.

### Conclusions

(1) Within the Yenisey Ridge processes of rock formation, ore deposition processes, and superimposed processes of alteration of older formations in the interval 1850 to 330 m.y. have been dated.

(2) The formation of the granites of the Taraksky massif in the Yenisey Ridge occurred in three main stages: the first,  $1850 \pm 100$  m.y. ago; the second, 1000 to 1300 m.y. ago; and the third about 400 m.y. ago.

(3) The interpretation and dating of superimposed processes is possible by analysis of ages based on various isotope ratios according to the lead method



and by comparing these ages with data on the isotopic composition of lead and with the results of dating by the argon method.

### *Acknowledgments*

We are grateful to N. P. Yermakov for **1** to **3** described in TABLE 2. We are also grateful to A. P. Vinogradov for his cooperation and assistance, without which this work could not have been completed.

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## Part II. Dating Sedimentary Rocks

### GLAUCONITE AS A POSSIBLE MEANS OF MEASURING THE AGE OF SEDIMENTS

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I present a brief progress report on the findings to date of work on glauconite. This is a progress report in a larger study of the dioctahedral micas that develop at or near the earth's surface.

Age measurements on glauconite by the K-Ar and Rb-Sr methods show a uniform variation with geological age with moderately small scatter. The results appear to fall 10 to 20 per cent short of ages measured on micas associated with dated igneous and sedimentary rocks in the time scale being assembled from the reports in this monograph. In no cases measured by my associates and myself have glauconites yielded ages that are definitely higher than the expected limits in the time scale.

Glauconites have interlayered structures. The interlayering involves mainly 10-Å layers and expandable (montmorillonitic) layers. The potassium content of glauconites is inversely proportional to the percentage of expandable layers. Furthermore, the percentage of expandable layers is greater in younger glauconite than in older. This suggests that the glauconite pellets continue to develop to purer mineral grains over long periods of time, with a decrease from 30 per cent or more of expandable layers in young glauconite to about 10 per cent in glauconite of early Paleozoic age. Almost without exception, Lower Paleozoic glauconite was found to contain more than 5 per cent potassium. As the expandable layers undoubtedly undergo some modification at depth and over long periods of time, it is to be expected that this factor alone will affect the age ratios.

Common strontium is adsorbed on basal plane surfaces of the expandable layers and is easily removed by an exchange. It is commonly roughly proportional to the abundance of these layers. It does not affect the Rb-Sr measurements, except in an increase of precision error in analysis. The only K-bearing mineral phase of importance that would be expected to be interlayered would be  $1M_d$  muscovite, although some  $2M_1$  detrital muscovite may be included in a glauconite grain as part of the aggregate. From work on illites it would be expected that the authigenic illitic phases would be equally retentive of argon as glauconite and not affect the age unless the illitic material underwent reorientation to  $1M$ , or possibly to  $2M$  types during diagenesis. This would have the same effect as an interlayered montmorillonite changing to glauconite with an increase in potassium with a loss of argon during the process. Thus if  $1M_d$  illitic material were present in the glauconite, it would be very difficult to determine whether the effect on argon age ratios during diagenesis were largely due to the glauconite or to the illitic material. Independent investigations currently being carried out on separated  $1M_d$  and  $2M_1$  muscovites from shaly sediments of Paleozoic age should give much information on this question.

Detrital  $2M_1$  muscovite in the clay size range included in the glauconitic aggregate would have the effect of increasing the age above that of the time of actual sedimentation. This might cause variability in the results, although thus far no ages have been observed that are definitely too high.

If the glauconite undergoes a slow purification with time, in which the expandable layers gradually become well-ordered glauconite, up to about 20 per cent of the mineral in Lower Paleozoic samples may not be truly authigenic. It is believed that this may be the cause of some of the lower ages. Superimposed upon this effect is an expected diffusion loss of argon in materials

TABLE 1  
GENERAL COMPARISON OF AGES OF GLAUCONITE BY DIFFERENT INVESTIGATORS  
TO DATE\*

Geological age	Lipson 1958	Wasser- burg <i>et al.</i> , 1956	Amir- khanov <i>et al.</i> , 1957	Kazakov & Pole- vaya, 1958	Goldich <i>et al.</i> , 1959	This laboratory†	
						K-Ar	Rb-Sr
Pliocene						7	
Miocene	20-33		20-26				
Oligocene	15-21		31				
Eocene	35		42-62	35		50-58	52-56
Paleocene	46	50		56		60	
Upper Cretaceous		68	73-83	72-112		87-90	67
Lower Cretaceous	136		83-104	88-122		88-104	
Jurassic			140	132			128-131
Triassic							
Permian				166		165	
Pennsylvanian				240		260	
Mississippian						284	
Devonian				323		330	303
Silurian			415			410	
Ordovician				447-458		414	355-445
Upper Cambrian		443			430-450	411-459	388-461
Middle Cambrian				400-610		346	440
Lower Cambrian						439	552
Sinian				707-900			

\* Calculated on the basis of decay constants:  $\lambda_K = 0.585 \times 10^{-10}$  years<sup>-1</sup>;  $\lambda_{Rb} = 4.72 \times 10^{-10}$  years<sup>-1</sup> for K 40; and  $\lambda_{Rb} = 1.47 \times 10^{-11}$  years<sup>-1</sup> for Rb 87.

† Includes earlier work of Cormier (1956) and Herzog *et al.* (1958).

that have been deeply buried, giving rise to unusually low values in some cases. However, in the normal cases of glauconite in thin sedimentary sections of the typical platform facies, the estimated diffusion loss of argon is too small to account for the observed decrease in age. The agreement of the Rb-Sr ages also bears out this conclusion.

Whatever mechanism is active in the lowering of the glauconite ages, it appears to be one that is universally present and also acts continuously with time because young samples show proportionately the same lowering in age, as do the older samples. A summary comparison of all measurements made by different investigators in the literature to date is shown in the accompanying TABLE 1.

From these data it is concluded that there is some consistent mechanism acting to lower the age of glauconites by 10 to 20 per cent. It appears that

this mechanism may be related to modifications in the structure of the glauconitic material in diagenesis and that this process continues with time. Superimposed on this rather uniform process is a variability that may be due in part to occluded detrital grains of  $2M_1$  muscovite or to argon loss by diffusion in those cases that have been deeply buried in folded sedimentary sections.

*Discussion of the Paper*

G. J. WASSERBURG (*California Institute of Technology, Pasadena, Calif.*): Do discrepancies on different materials from the Cambrian really exist?

G. H. CURTIS (*University of California, Berkeley, Calif.*): In that regard, my associates and I have four runs on Lower Cambrian glauconite from the *Olenellus* zone and did K-Ar analysis in mountains where the glauconite has suffered the Laramide orogeny. The date is  $400 \pm 10$  million years (m.y.). These samples are Lower Cambrian, thousands and thousands of feet below most of these others. They must be much older than yours. This fact is not a discrepancy with previous time scales.

HURLEY: The work of Curtis and Evernden and others very nicely demonstrates argon loss in deeply buried glauconite. There are some very low ages presented in the table that are well explained by the deep burial of the material. I think if you keep to the very flat-lying, thin-bedded platform facies, you will find that the glauconite ages are more consistent.

G. R. TILTON (*Carnegie Institution of Washington, Washington, D.C.*): In regard to Wasserburg's question, in so far as I know there are no decent dates in the Cambrian with which the glauconite results may be compared. Such comparisons as exist in the middle part of the time scale can occasionally be satisfactory. However the Ordovician points are the most bothersome. There are now results of 450 m.y. for the Middle Ordovician, which coincides with the ages obtained on Cambrian glauconites.

WASSERBURG: Where are the 450's?

TILTON: They are dealt with elsewhere in this monograph.

WASSERBURG: At least until today, no discrepancies have been presented with the lower Paleozoic ages.

R. E. FOLINSBEE (*University of Alberta, Edmonton, Alberta, Canada*): I shall mention that in your last report, Hurley, you had a number of Ordovician and Cambrian glauconites, K-Ar and Rb-Sr ages. I plotted those out putting Ordovician and Cambrian against dates, by obtaining quite a scatter of points. The maximum age that generally could be assigned is in pretty good line with Middle Ordovician bentonite age (450 m.y.) but, if you plotted the average age, you would miss it by quite a margin.

HURLEY: That is correct. The scattered ages do come up to a line that is close to the present estimated time scale.

WASSERBURG: I shall make a comment about mineral separation procedures in processing glauconites. By careful hand picking, it is possible to obtain highly radiogenic strontium from Cambrian glauconites without resorting to an acid leaching procedure.

H. FAUL (*United States Geological Survey, Washington, D.C.*): I wonder whether the most important factor here is not fixing of potassium by glauconite in a variable proportion with time.

CURTIS: I have a comment on this in regard to these 400-m.y. dates. It is thought that at this time this glauconite was fixed by orogeny into a very, very high-grade illite. It has an illite structure. It is the highest potassium glauconite reported in the literature, and from that report we think it held argon because this is exactly the same age obtained on the intrusions in the immediate area.

QUESTION: No exchange?

CURTIS: I have forgotten the figure, but it is the highest in the literature.

QUESTION: Higher than 7.5 per cent?

CURTIS: Yes, more than 7.5 per cent higher than any other reported glauconite, and the structure is an illite. It is right beside intrusions that are dated at more than 360 m.y. Thus it has held all accumulated argon from that time and possibly has held a small amount of other argon.

## UTILIZATION OF GLAUCONITE IN ABSOLUTE DATING

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Until recently, estimates of the duration of geologic events in the earth's development were made exclusively by determining the age of minerals of intrusive rocks. This introduced a certain degree of uncertainty even in cases where a lower age limit for the intrusion could be established with fair precision from its penetration of faunally characterized sedimentary strata. As a rule the upper age limit, which is determined from the presence of pebbles of igneous rocks in overlying sediments, is by no means always fixed and is usually considerably removed in time from the "moment" of formation of the intrusion.

Thus absolute dating of geological subdivisions from intrusive rocks is only an approximate estimate of time intervals between individual stages and phases of magmatism.

In view of this fact, it is extremely desirable to correlate absolute geochronology with the generally accepted biostratigraphic scale by directly determining the age of those geologic formations that contain mineralized faunas or floras.

The possibility of such a correlation appeared with the development of the argon method through the utilization of authigenic glauconites, syngenetic with biostratigraphically dated sedimentary strata as the material for age determinations.

The extensive—in fact, almost universal—distribution of glauconites in time and space and the synchronism of their formation with that of marine sediments in the process of diagenesis, open to the argon method a real possibility of determining by glauconites the age of sedimentary formations over a wide range of geologic time.

Determinations of absolute age by glauconites with the argon method have been the subject of a comparatively small number of papers in Soviet and other foreign journals: M. M. Rubinshteyn,<sup>8</sup> Kh. I. Amirkhanov *et al.*,<sup>1</sup> Wassergburg *et al.*,<sup>13</sup> Lipson,<sup>11</sup> Kh. I. Amirkhanov *et al.*,<sup>2</sup> L. N. Ovchinnikov *et al.*,<sup>6</sup> Lipson,<sup>12</sup> Curtis and Reynolds,<sup>10</sup> G. A. Kazakov and N. I. Polevaya,<sup>4</sup> N. I. Polevaya *et al.*,<sup>7</sup> and others.

The first attempt to determine the age of glauconites by the strontium method was made by Cormier *et al.*<sup>9</sup>

The published results attest to the possibility of obtaining rather reliable ages for glauconites by the argon method.

At present, however, there is still some doubt of the reliability of the results obtained, since the results of a small number of systematic investigations concerned with studies of the degree to which radiogenic argon is retained in glauconites have proved contradictory.

Glauconite is very similar in structure to micas and, by analogy with them, radiogenic argon might be expected to be tightly bound. However Kh. I. Amirkhanov *et al.*,<sup>3</sup> in a study of the removal of argon from glauconites upon heating, determined that there was a considerable loss (up to 20 per cent) of this mineral at temperatures as low as 100° C., which they attributed to



desorption. This led them to the conclusion that radiogenic argon is loosely bound to glauconite.

We have repeated these authors' experiments and have studied the character of the removal of argon from glauconites upon heating for samples with granules of various dimensions (from greater than 0.25 mm. to less than 0.01 mm.).

Nevertheless we have not observed argon removal from glauconites at 100 to 200° C. We suspect that a systematic error has occurred in the experiments of the authors mentioned, which leads them to incorrect conclusions.

As is evident from FIGURE 1, in which curves of argon removal from two samples are presented, the removal of argon begins at practically the same point as the liberation of chemically combined water. On the other hand, removal of adsorbed water from glauconite is not accompanied by the removal of argon. In this connection, the dimensions of the grains of the sample have no effect on the character of argon removal. All of this causes us to believe that liberation of radiogenic argon from glauconites occurs only when the crystalline lattice is destroyed and is not connected with processes of desorption. Consequently, in the absence of processes that disrupt the crystalline lattice of glauconites, we may expect that argon will be tightly bound within them over long intervals of geologic time.

However the mobility of argon is not the only possible cause of a shift in the  $\text{Ar}^{40}/\text{K}^{40}$  ratio in glauconites. As is well known, the adsorption properties of glauconites and their marked tendency to cation exchange lead to great variations in their chemical composition. We have attempted to estimate the role of cation exchange in glauconite in relation to changes in potassium content and, at the same time, to trace the effect of cation exchange on the retention of radiogenic argon in glauconite. If the exchange in glauconite is not just a surface process but also involves ions in the lattice, such a reaction can cause a loss of argon from the mineral. The difficulty of determining the time of occurrence of such exchange reactions in nature could be a serious obstacle to obtaining reliable values for absolute ages from glauconites.

Our investigations in this area have just begun, and for that reason they encompass only a small number of variations in reaction conditions and a small number of glauconite samples. Consequently our results may be regarded as preliminary only. Experiments were carried out on three samples of glauconite isolated in pure form; these samples represented the dark-green variety of this mineral. The cation-exchange reaction was carried out by standard procedures at room temperature.<sup>13</sup>

The minerals were successively treated with hydrochloric acid of a given concentration and then with solutions of potassium chloride and calcium chloride, to complete saturation with the respective cations. The concentrations of solutions in these experiments varied between 0.05 and 0.5 N. As a result of this treatment of glauconites with solutions of the corresponding cations, they were transformed successively into the H-form, the K-form, and the Ca-form. Potassium and argon concentrations were determined both in the original mineral and in its calcium form. In addition, potassium was determined in the K-form of glauconite samples subjected to investigation.

As may be seen from the results obtained (TABLE 1), the argon content in all samples subjected to treatment with solutions remained constant within

the limits of accuracy of the experiment. This permits us to conclude that the potassium in the crystalline lattice of glauconite does not participate in the cation exchange.

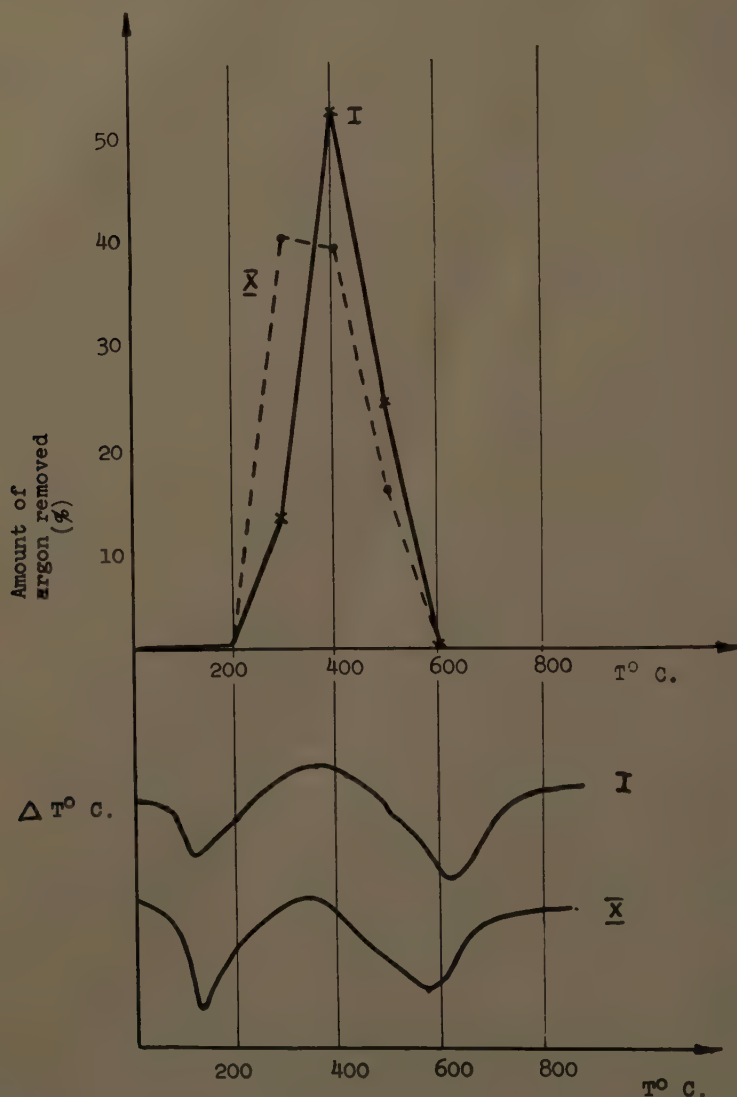


FIGURE 1.

In TABLE 2 data are shown on the potassium content of two glauconite samples in the various stages of treatment. From the data obtained we may determine the changes in potassium content resulting from adsorption by the mineral from solution. As is evident from the table, under these experimental conditions the amount of adsorbed potassium came to 13 per cent of the total

potassium content of the glauconite. In view of this fact, it was of interest to determine the probability of the presence of appreciable amounts of adsorbed potassium in glauconite. For this purpose potassium was determined in a series of glauconite samples before and after treatment with 0.05 N HCl.

TABLE 1  
EFFECT OF CATION EXCHANGE ON ARGON RETENTION IN GLAUCONITE

Sample	Concentration of working solutions	Amount of adsorbed HCl (mEq./100 gm. glauconite)	K content (%)		Ar content (cm. <sup>3</sup> /gm.)	
			Before treating	After treating	Before treating	After treating
186-V	0.05N	19	5.70	5.60	0.246	0.242
1	0.1N	22	6.06	5.75	0.170	0.170
B	0.1N	36	6.65	6.55	1.340	1.350
186-V	0.5N	22	5.70	5.78	0.246	0.242

TABLE 2  
DATA ON CATION EXCHANGE IN GLAUCONITE

Sample	K content (%)				Content of exchanged K in relative % under given experimental conditions
	Before treating	H-form	K-form	Ca-form	
B	6.06	5.75	6.50	5.75	13.0
1	6.65	6.50	7.0	6.55	7.5

TABLE 3  
DATA ON DESORPTION OF POTASSIUM FOR CERTAIN GLAUCONITE SAMPLES

No.	Site	Age (million years)	Potassium content		Relative change in potassium content (%)	Adsorptive capacity of glauconite (mEq./100 gm. glauconite)
			Before treating	After treating		
(1)	Ciscaucasia, Umantsevo hole	37	5.31	5.31	0	4
(2)	Czechoslovakia, Koberzhik (A)	76	5.60	5.63	+0.5	20
(3)	Czechoslovakia, Koberzhik (B)	77	6.06	5.75	-5.2	36
(4)	Kaluga oblast, Bukan'skoye deposit	80	5.78	5.77	-0.2	12
(5)	Georgia, Inguri River	90	5.68	5.74	+1.0	12
(6)	Caucasus, Great Laba River, Skryleyeva Ravine	105	5.72	5.63	-1.9	12
(7)	Estonia, Maardu deposit (1)	467	6.65	6.55	-1.5	22
(8)	China, Hopch Province (186-V)	890	5.70	5.68	-0.3	19

As may be seen from TABLE 3, in glauconites with different adsorption capacities, changes in potassium content were relatively small or completely absent, and the corrections introduced into the calculated ages should be insignificant.

The problem requires further study, however, since on the basis of our data we cannot completely deny the probability of the presence of a perceptible

amount of adsorbed potassium in glauconite; but the theory of cation exchange permits us to speak of the existence not of an absolute but of a relative value of exchange capacity depending on the surroundings, the concentrations and pH of solutions, and various other factors.

The possibility that excess argon, trapped in the process of formation of the mineral from sea water, is present in the glauconite seems rather unlikely to us. However distortion of the age ratio  $\text{Ar}^{40}/\text{K}^{40}$  may take place in those cases in which glauconite is not completely free of admixture of terrigenous material containing potassium. In this case, the greater the difference between the age of the glauconite and the age of the material of admixture the greater will be the error in dating the glauconite.

Accordingly, we subjected not only isolated glauconite but also whole rock to analysis. According to the first preliminary data (TABLE 4) a noticeable

TABLE 4  
EFFECT OF TERRIGENOUS IMPURITIES ON  $\text{Ar}/\text{K}$  RATIO IN GLAUCONITE

No.	Sample	K (%)	$\text{Ar}^{40} (\times 10^{-7} \text{ gm./gm.})$	$\text{Ar}/\text{K}$	Age (m.y.)	Remarks
XIX	Belaya River, Caucasus, glauconite	6.35	0.407	0.0053	93	Impurities in glauconite consist mainly of quartz
XX	Same location, glauconite-containing rock	4.52	0.260	0.0049	86	
IV	Serdobsk hole 2r glauconite	6.12	3.84	0.0511	749	Impurities essentially feldspathic
Sample 1	Same location, glauconite-containing rock	2.88	2.43	0.0700	964	

distortion of the  $\text{Ar}^{40}/\text{K}^{40}$  age ratio was found only in a sample with very fine, unseparated particles of feldspar. Thus purity of the glauconite taken for analysis is one of the conditions for obtaining reliable age values.

The results of these investigations indicate that glauconite can be a completely suitable mineral for absolute dating. However these investigations do not cover all the possible variety of factors tending to distort the  $\text{Ar}^{40}/\text{K}^{40}$  age ratio in glauconite under natural conditions. Therefore we are not yet able in every instance to give a well-founded estimate of the reliability of the ages obtained in each actual case.

#### *Results of Dating of Glauconites*

With the help of a considerable number of geologists, a large collection of samples of glauconite-containing rocks was gathered, representing in stratigraphic cross-section almost all geological formations from Upper Proterozoic to Upper Paleogenic.

All the glauconites studied (around 100 samples) were taken from sedimentary strata; in the majority of instances these strata had reliable biostratigraphic dates. Some samples were taken from cores obtained by supportive drilling; the others were taken directly from outcrops. The various glauconite samples differed from each other rather markedly in both composition and

external characteristics. Among the samples analyzed by us, all the color varieties of glauconite from dark olive green to pale green were represented. The samples also differed as to the dimensions of their granules (from rather large granules of about 1 mm. in diameter to pelite granules).

Ages were determined by the argon method. Potassium was determined by the dipicrylamine method, with preliminary solution of the sample in a mixture of hydrofluoric and sulfuric acids. Argon was determined by the volumetric method; the radiogenic purity of the isolated argon was tested with a mass spectrometer.

In calculating ages the following values of the potassium decay constants were used:  $\lambda_K = 0.557 \times 10^{-10} \text{ year}^{-1}$  and  $\lambda_\beta = 4.72 \times 10^{-10} \text{ year}^{-1}$ .

The selection and mineralogic study of the material and separation of one-mineral fractions was carried out in the Institute of Geochemistry and Analytical Chemistry, Academy of Sciences of the U.S.S.R. in Moscow by G. A. Kazakov. All the experimental work on the determination of the absolute age was done in the All-Union Geological Scientific Research Institute in Leningrad. In the experimental work, V. D. Sprintsson and L. V. Shashukova assisted us.

#### *Cenozoic and Mesozoic*

For a number of samples of Tertiary and Cretaceous glauconites, ages were obtained that were in excellent agreement with each other. These data are presented in TABLE 5, from which it is evident that a somewhat greater spread in ages was obtained for only two samples of Lower Cretaceous age. According to these preliminary data the boundary between the Mesozoic and the Cenozoic is found roughly in the interval 60 to 70 m.y., and the boundary between the Cretaceous and Jurassic at about 135 m.y., which does not contradict the data of other authors or the scale of Holmes. However, for a definitive determination of the boundaries of the subdivisions of the Cenozoic and the Mesozoic, these data are not enough. Work in this direction is therefore continuing on glauconite samples from deposits in the Mesozoic and Cenozoic of the Russian and Siberian Platforms, Turgay, the Caucasus, and Central Asia.

#### *Upper and Middle Paleozoic*

The segment of geologic time between 130 and 400 m.y.—that is, from Middle Mesozoic to Lower Paleozoic—has not been studied sufficiently by us, the data (TABLE 6) obtained on the small number of glauconite samples of this age are not as yet in satisfactory agreement with each other and with the scale of approximate geologic time, and more determinations will have to be made for the sake of accuracy.

There is no doubt, however, that the age boundaries of the subdivisions of the Upper and Middle Paleozoic must be greatly lowered in comparison with the scale of Holmes.

At present a large number of glauconite samples that have been accurately dated paleontologically (from Upper Permian to Ordovician) have come into our possession, and work on pinpointing the age boundaries of the Upper and Middle Paleozoic is continuing.



TABLE 5

## ABSOLUTE AGE DATA FOR MESOZOIC-CENOZOIC GLAUCONITES\*

System	Division	Site	Imbedding rocks	K (%)	$A_{140}/K^{40}$	Age (m.y.)	Geologic age /	Data of other authors for glauconites
Neogene	Miocene							22-27 <sup>1</sup>
	Oligocene							18-32 <sup>11,12</sup>
		Ciscaucasia, Umantsevo hole No. 54, depth of 310 m. (combined Caucasus expedition)	Sandstone	5.31	0.0021	37	Kiev stage	33 <sup>1</sup>
		Volga River area. Stalingrad hole 4077, depth of 119 m. (combined Caucasus expedition)	Clayey sandstone	5.48	0.0026	46	Kiev stage	43-64 <sup>1</sup>
		Turgay (B. Mikhaylov)	Sandstone	4.99	0.0029	51	Tassaranskaya suite of Middle Eocene	48 <sup>13</sup>
		Abkhazia, Kodori River (G. A. Kazakov)	Limestone	6.99	0.0030	53	Upper layers of Paleocene	60 <sup>9</sup>
		Daghestan, Ullu-Chay (G. A. Kazakov)		4.62	0.0038	70	Datsky stage	34-35 <sup>11,12</sup>
		Volga River area, Saratov, Lysaya Hill (L. Kornetova)	Marl	6.02	0.0045	79	Senon	
		Czechoslovakia, Koberzhik hole, depth of 76-77 m. (Brezina)	Sandstone	5.96	0.0044	78	Kon'yak (Cognac)	44 <sup>2</sup>
		Czechoslovakia, Koberzhik hole, depth of 77-78 m. (Brezina)	Sandstone	6.00	0.0045	79	Senomanian	
Cretaceous		Czechoslovakia, Melnyk district, Koshatki deposit (M. Mashka)	Sandstone	4.42	0.0053	93	Senomanian	76-78 <sup>1</sup>
		Kaluga oblast, Bukanskoye deposit (B. N. Gimelfarb)	Sandstone	5.78	0.0045	80	Senomanian	89 <sup>1</sup>
			Sand	4.29	0.0057	100	Senomanian	94 <sup>3</sup>
		Northern Caucasus, Great Laba River, Skryleyeva Ravine (G. A. Kazakov)	Aleurolite	5.72	0.0059	103	Albian	70 <sup>13</sup>
		Northern Caucasus, Great Laba River, Skryleyeva Ravine (G. A. Kazakov)	Clayey sandstone	6.35	0.0053	93	Aptian	62-70 <sup>9</sup>
		Northern Caucasus, Belaya River (G. A. Kazakov)	Clayey sandstone	5.00	0.0061	107	Aptian	
		Northern Caucasus, Baksan River (G. A. Kazakov)	Aleurolite	5.68	0.0053	93	Aptian	89-100 <sup>1</sup>
		Georgia, Inguri River (G. A. Kazakov)	Limestone	5.28	0.0053	93	Barremian	100-139 <sup>1</sup>
		Moscow, Lenin Hills (G. A. Kazakov)	Sandstone	5.23	0.0079	136	Neokom	130 <sup>11,12</sup>
		Moscow oblast, Yegor'yevsk deposit, from drill-hole (Ts. I. Uflyand)	Limestone	4.91	0.0077	133	Volga stage (subphosphoric layer)	100 <sup>1</sup>

\* All data from Soviet authors have been recalculated on the basis of new values of the potassium decay constants:  $\lambda_{40} = 0.557 \times 10^{-10}$  year<sup>-1</sup> and

*Lower Paleozoic and Upper Proterozoic*

The estimation of geologic age and the correlation of sedimentary strata becomes much more complex when we go below the "Olenellus biozone" since comparison on the basis of spores, algae, helminths, and stromatolites is still not sufficiently developed.

We consider the data obtained for glauconite from the late Pre-Cambrian deposits of the various areas of the U.S.S.R. to be of particular interest and deserving of further detailed examination. With the help of geologists, we have been fortunate in obtaining a unique collection of glauconite samples, collected both from outcrops and from supportive-drilling holes. For certain areas age data have already been obtained for the stratigraphic cross section from the Ordovician to the Upper Proterozoic inclusive. The results obtained are considered separately below for each of the areas studied.

TABLE 6  
UPPER AND MIDDLE PALEOZOIC

Site	K (%)	Ar <sup>40</sup> /K <sup>40</sup>	Age (m.y.)	Geologic age
(1) Northern Timan, Indiga River (V. P. Barkhatova)	4.62	0.0164	274	Lower Permian, Sakmara stage
(2) Dergunovka hole, depth of 1822 m.	5.29	0.0186	308	Middle Carboniferous, Moscow stage, Vereya Horizon
(3) Voronezh massif, hole on side toward Lezhen'ki	6.78	0.0206	334	Upper Devonian, Fransky stage, Voronezh layers

*Russian Platform*

TABLE 7 presents the results of determinations of the absolute age of glauconites from sedimentary strata of the Ordovician, Lower Cambrian, and the most ancient horizons of the sedimentary cover of the Russian Platform. The absolute ages for faunally characterized Lower Ordovician (upper portion of the Tremadoc stage) were very similar and vary within the interval 460 to 470 m.y.

An especially important fact is the confirmation by the argon method of a break in the deposits between the Lower Ordovician and the Lower Cambrian, which was discovered by Ye. P. Burns in studying a core sample from hole No. 2 in the village of Kupa (Belorussian S.S.R.) at a depth of 180 m. Above 180 m. lie sandstones with fauna of the genus *Orthis* (age of glauconite at a depth of 175 m. is 460 m.y.); below this level lie blue clays of the Baltic complex containing fauna of the genus *Olenellus* (age of glauconite taken from a depth of 257 m. is 540 m.y.).

For glauconite samples from nonfossiliferous sedimentary strata of the Ryazan'-Pachelma depression lying below the blue clays much greater ages were obtained, presumably attesting to a pre-Paleozoic (Sinian) age. We obtained ages of 598 and 606 m.y. for the upper glauconite blocks, and 723 to 770 m.y. for the lower glauconite blocks (Pachelma suite of Serdobsk series).

Glauconite taken from the boundary with the Kaverinskaya suite lying beneath this was found to be even older (898 and 943 m.y.). Finally, a glau-

TABLE 7

	Site	Imbedding rock	K (%)	Ar/K	age (m.y.)	Presumptive geological age
Ordovician	Estonian S.S.R., Maardu deposit, mine drift No. 5 (Kurman, I.M.)	Sandstones with fauna	6.65	0.0297	470	Lower Ordovician
Lower Cambrian	Belorussian S.S.R., hole R-2, depth 175 m. (Ye. P. Bruns)	Clayey sandstones with fauna <i>Orthis</i>	6.78	0.0290	460	Lower Ordovician
	Same location, depth 257.8 m. (Ye. P. Bruns)	Sandstone streaks in clays	4.66	0.0347	540	Baltic series; blue clays of Lower Cambrian
Cambrian(?) Pre-Cambrian(?)	Ryazan, Pachelma depression, Lipvagi, hole R-1, depth 1429 m. (I. Ye. Postnikova)	Sandstones	5.84	0.0384	587	Valday series (according to I. Ye. Postnikova, the laminarite suite)
	Serdobsk, hole R-2, depth 1380 m. (I. Ye. Postnikova)	Sandstones with pollen remnants of <i>Palaeophrosaccus alatus</i> Naum., <i>Palaeophrosaccus porosus</i> Naum., <i>Phosphosphaera laminatilis</i> Naum.	5.33	0.0394	600	Valday series (according to I. Ye. Postnikova, the laminarite suite)
	Serdobsk, hole R-2, depth 1758 m. (M. M. Tolstikhina)	Sandstone	4.90	0.0492	726	Serdobsk series
	Serdobsk, hole R-2, depth 1787 m. (I. Ye. Postnikova)	Sandstones with pollen remnants of <i>Brochosaccus antiquus</i> Naum., <i>Phosphosphaera notata</i> Naum.	6.12	0.0506	743	Serdobsk series
	Zubova, Polyana, depth 1377 m. (Z. P. Ivanova)	Lower portion of Pachelma Suite, near contact with Kaverinskaya Suite	6.49	0.0527	767	Serdobsk series
	Pugachev, hole 10, depth 1850-1870 m. (V. D. Shutov)	Lower portion of Pachelma Suite, near contact with Kaverinskaya Suite	4.26	0.0530	770	Serdobsk series
	Kaverino, hole 1, depth 1597-1609 m.	Lower portion of Pachelma Suite, near contact with Kaverinskaya Suite	5.80	0.0680	943	Serdobsk series
	Pugachev, hole 10, depth 2161 m. (V. D. Shutov)	Lower portion of Pachelma Suite, near contact with Kaverinskaya Suite	3.90	0.0640	898	Serdobsk series
	Cisuralia, Serafimovskaya hole 119, depth 2898 m. (Lagutenkova)	Lower portion of Pachelma Suite, near contact with Kaverinskaya Suite	6.31	0.103	1290	Serdobsk series

conite sample from the Lower Bavlinskaya suite of the Volga-Uralian depression gave the oldest age (1290 m.y.), although at present the majority of geologists consider this suite to be parallel with the Serdobsk series.

In addition, a number of determinations of absolute age of glauconites from ancient deposits of the northern margin of the Russian Platform were also made (hyperborean part of the Murmansk-Kola region), which are apparently of the same age as the sparagmite formation of Norway and the Sinian of China and are usually considered parallel with deposits of the Serdobsk series. The data cited in TABLE 8 are in excellent agreement with these concepts, as well as with the data of E. K. Gerling (1000 to 1035 m.y.) as mentioned elsewhere in this monograph.

*Western Slope of Southern Urals (Bashkir Anticlinorium)*

The sedimentary rocks of the Bashkir Anticlinorium are a classical cross section of the late Pre-Cambrian and were classified by N. S. Shatsky as of the Rhiphean group.

TABLE 8  
HYPERBOREAN GLAUCONITES FROM DEPOSITS OF MURMANSK-KOLA REGION

Site and author	K (%)	Ar <sup>40</sup> /K <sup>40</sup>	Age (m.y.)
Middle of peninsula, M. Volokovaya Gulf (B. M. Keller)	5.90	0.0610	865
Middle of peninsula, M. Volokovaya Gulf (B. M. Sokolov)	6.21	0.0775	1040
Middle of peninsula, M. Volokovaya Gulf (B. M. Sokolov)	6.93	0.0790	1059
Kildin Island (B. M. Keller)	5.89	0.0645	904
Kildin Island (B. M. Sokolov)	4.50	0.0750	1018

The age of these ancient nonfossiliferous strata is currently the subject of lively and violent discussion between representatives of different schools of stratigraphers, structural geologists, and lithologists.

Schematically, the classical cross section of the Rhiphean deposits of the Urals can be represented as follows. At the base of the cross section on the Ratashsky Archean gneisses, with erosion and angular unconformity, lie the deposits of the Burzyanskaya series and upon this the deposits of the Yurmatinskaya series. After a discontinuity, with considerable erosion and basal conglomerates, the five suites of the Karatauskaya series lie upon the Yurmatinskaya series: Zilmerdaskaya, Katavskaya, Inzerskaya, Minyarskaya, and Ukskaya (from bottom to top).

The Ukskaya suite is thus the last in the cross section of the Rhiphean group. Above it lies the Ashinskaya suite (also with a discontinuity), the age of which, thus far, is unfortunately one of the most disputed questions in the geology of the Urals. Some investigators regard it as Devonian, some as Silurian or Ordovician. However, an increasing amount of factual material has accumulated recently suggesting a Cambrian or possibly even a Pre-Cambrian age for the Ashinskaya suite.

We have analyzed seven samples of glauconite from the various suites of this highly interesting cross section. The results of the age determinations on

these samples, shown in TABLE 9, indicate the closeness in time of the Rhiphean deposits of the Urals and the sedimentary cover of the Russian Platform.

The most ancient is the glauconite from the Avzyanskaya suite (upper layers of the Yurmatinskaya series), its age being very close (1263 m.y.) to that of the Lower Bavlinskaya suite.

The age of the Karatauskaya series (616 to 932 m.y.) is also readily shown to be parallel with that of the Serdobsk series of the Russian Platform (606 to 943 m.y.), which completely substantiates the geologic concept that their ages are the same.

TABLE 9  
AGE OF GLAUCONITES FROM ANCIENT STRATA OF THE SOUTHERN URALS

No.	Site	Imbedding rock	K (%)	Ar <sup>40</sup> /K <sup>40</sup>	Age (m.y.)	Suite
(1)	Kiselyov spring, on the road between Asha and Min'yar, Asha River (I. Ye. Postnikova)	Sandstone	5.79	0.0372	572	Lower portion of Ashinskaya suite
(2)	Zillim River Basin, Kamyshta area (Yu. R. Bekker)	Close-grained sandstone	5.00	0.0407	618	Ukskaya suite
(3)	Bassa River Basin, Kulmys area (Yu. R. Bekker)	Close-grained sandstone	6.14	0.0405	616	Ukskaya suite
(4)	Min'yar area (Yu. R. Bekker)	Close-grained sandstone	3.55	0.0520	760	Lower layers of Min'yar'skaya (min'yar suite) (Minsk stratum)
(5)	Urta-Airy River, Nugush River Basin (N. P. Verbitskaya)	Close-grained sandstone	4.45	0.0620	876	Inzerskaya suite
(6)	Lake Min'yar, hole 18 (I. Ye. Postnikova)	Quartzitic sandstone	5.90	0.0680	932	Lower layers of Inzerskaya suite
(7)	Great Katav River, 10.5 km. above Zaprudovka (N. P. Verbitskaya)	Quartzitic sandstone	5.85	0.1000	1263	Avzyanskaya suite (upper layers of Yurmatinskaya series)

The age of the overlying Ashinskaya suite (573 m.y.) was found to be very close to that of the upper suite of the Karatauskaya series 616 m.y., which leads us to express the opinion that the unconformity between the Ukskaya and the Ashinskaya suites is not so considerable in terms of time and that perhaps the Ashinskaya suite is of a Lower Cambrian age.

#### *Siberian Glauconites*

Of the samples at our disposal, we have analyzed thus far only six from the ancient strata of the Aldan shield, the Yenisey ridge, and the western framework of the Aldan shield. The results are shown in TABLE 10.

#### *Chinese Platform*

It was of the greatest interest to compare ages for glauconites from ancient deposits of the Russian Platform, the Murmansk-Kola region, the Urals, and Siberia with the absolute age of glauconites from classical cross sections of



Sinian deposits of the Chinese Platform. This material was kindly submitted to us by Chen Yü-Ch'ih and Yeh Lien-Chü.

Four samples were analyzed, and the results of the age determinations on these samples are given in TABLE 11.

As may be seen from the table, the age of the Mantou suite determined from glauconite was close to the age of the Zherbinskaya suite of the Aldan stage, beneath which lies the thick, faunally uncharacterized Yudomskaya suite, which is also a part of the Aldan stage. The discovery of fauna of the genus *Red-*

TABLE 10  
GLAUCONITES FROM SIBERIA

No.	Site	Geological age	K (%)	Ar <sup>40</sup> /K <sup>40</sup>	Age (m.y.)
(1)	Lena River, near mouth of Patoma River (L. I. Salop)	Lower Cambrian (Zherbinskaya Suite of Aldan stage)	6.23	0.0320	502
(2)	Ushakovka River (Isakova)	Motskaya suite of Aldansky Layer	3.41	0.0400	609
(3)	Teya River, Yenisey Ridge (M. S. Semikhatov)	Chividenskaya suite	5.28	0.0510	747
(4)	Lower Tunguska River (V. I. Dragunov)	Suite of drillhole (?) (Upper Proterozoic)	4.42	0.0665	925
(5)	Yenisey Ridge (M. A. Semikhatov)	Pogoryuyskaya suite of Proterozoic	4.09	0.0870	1140
(6)	Anabar River Ulakhan-Yut-teekh Olenyok upheaval (I. V. Pokrovskaya)	Sololiyskaya suite (Sinian)	2.77	0.1000 0.0995	1263 1260

TABLE 11  
AGE OF ANCIENT DEPOSITS IN THE CHINESE PEOPLE'S REPUBLIC

No.	Site	Geological age	K (%)	Ar <sup>40</sup> /K <sup>40</sup>	Age (m.y.)
Kr-462	Hsinshan, Wutai district, south of Chukuangssu Shanghsi Province	Mantou suite C <sub>m</sub>	6.41	0.0330	516
Kr-186A	Chi district, Chinenhyu Ho-peh Province, Block A	Chinerhyu horizon, 10th division of the Sinian	5.52	0.0617	873
Kr-186V	Chi district, Chinenhyu Ho-peh Province, Block V	Chinerhyu horizon, 10th division of the Sinian	5.70	0.0633	890
K-1	Hoyajangchu, Pinuchun district, Hopeh Province	Fourth division of the Sinian: manganese-bearing horizon	2.48	0.0774	1040

*lichia* in deposits of the Mantou suite gives us reason to suppose that the boundary between the Sinian and the Lower Cambrian must be assigned an age below 500 m.y. since this genus is not characteristic of the very lowest layers of the Cambrian.

In this connection our attention is drawn to the very old ages for Sinian glauconites (870 to 890 m.y.) from the uppermost horizons of the Sinian period. On the basis of these data we may express the view that a considerable discontinuity occurs between the deposits of the Sinian and the Cambrian. There can be absolutely no doubt that this work must be continued since the data thus far obtained are few; to draw any serious geologic conclusions whatever from them would be premature.

*Conclusions*

Our attempt to reconcile absolute and relative geochronologies by utilizing glauconite samples syngenetic with the sediments containing them for absolute dating can be regarded as largely successful. The data obtained for the Mesozoic, Cenozoic, and Lower Paleozoic-Upper Proterozoic seem to us to be rather reliable and indicate the great possibilities of the argon method. For the first time values have been obtained in the interval from 500 to 1300 m.y. for the ages of the oldest sedimentary formations of the Russian Platform, the Urals, and Eastern Siberia. Thus the "blank space" in absolute geochronology (from Jotnian to Cambrian) is beginning to be deciphered to some extent.

One of the paramount problems in the present work is obtaining new data for the most ancient nonfossiliferous sedimentary formations, for which age classification and correlations are very complicated.

We have made considerably less progress in the area of the Upper and Middle Paleozoic because of the lack of reliably dated material. In view of the disagreement that has arisen with the existing scale of absolute geochronology for the time interval from the Lower Permian to the Silurian, we regard it as essential for these data to be obtained for a number of different regions.

It would appear that utilization of glauconite for absolute dating may, in the future, provide substantial assistance in pinpointing the boundaries of geologic subdivisions and also in correlating nonfossiliferous sedimentary formations.

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## DATING OF BLACK SHALES\*

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As absolute chronometers, black shales can hardly be improved upon in so far as correlating them with the fossil record is concerned. Possibilities for absolute dating arise because uranium is frequently enriched in these formations.

The first question that should be asked is whether uranium was precipitated during formation of the sediment. The best evidence that uranium is syngenetic, at least in bituminous marine black shales, lies in autoradiographic studies. These show alpha tracks to be evenly distributed with no evidence of clustering, indicating uranium-bearing crystals or veins. Uranium is thought to occur as coatings on clays and organic particles and was probably precipitated from sea water under reducing conditions.

Studies on uranium-lead dating have been conducted on two formations: the Upper Devonian Chattanooga shale of the eastern United States, and the Upper Cambrian Swedish alum shale. FIGURE 1 shows a sketch of an outcrop of the Swedish alum shale. The black shale has about 25 per cent organic material and 100 to 200 ppm uranium. The tiny lenses called Kolm occur in two horizons. They have 75 per cent organic material and about 5000 ppm uranium. The Kolm is especially valuable for study because three uranium-lead isotopic ages can be calculated. On the shale, only the  $U^{238}/Pb^{206}$  age can be calculated with accuracy. The common lead correction causes large errors in the  $U^{235}/Pb^{206}$  and  $Pb^{207}/Pb^{206}$  ages.

TABLE 1 presents some apparent ages found for the Swedish shale and Kolm. In the Kolm, the discordance is striking, but there is, by and large, consistency in the apparent age found in different samples. Altogether, 24 samples have been run. The majority have isotopic ages closely similar to S-14, S-15, and S-19 in the table. Samples S-24 and S-25, therefore, represent a divergence from the average age.

The shales, all of which were sampled close to Kolm lenses, show apparent ages in an inverse relation to those of the Kolm. The shale shows high  $U^{238}/Pb^{206}$  ages and low  $Pb^{207}/Pb^{206}$  ratios. This difference suggests movement of some element in the  $U^{238}$  decay chain from the Kolm to the shale. The result is that some radiogenic  $Pb^{206}$  from the Kolm is now in the shale and, of course, this results in the disparity in the  $U^{238}/Pb^{206}$  and  $Pb^{207}/Pb^{206}$  ratios between the shale and Kolm. The separation of isotopes in the  $U^{238}$  chain from those in the  $U^{235}$  chain is possible because there is a great difference in the respective half lives of the isotopes. For example,  $Ra^{226}$  in the  $U^{238}$  decay chain has a half life of 1620 years while  $Ra^{223}$  in the  $U^{235}$  chain has a half life of 12 days. Leaching solutions, therefore, have a much greater chance of removing  $Ra^{226}$ .

TABLE 2 compares the isotopic age with the present state of equilibrium in several samples. The activity of 80,000-year  $Th^{230}$ , 1620-year  $Ra^{226}$  and 22-year  $Pb^{210}$  is compared to that of  $U^{238}$ .

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$\text{Ra}^{226}$  was measured by counting its radon daughter in an alpha ionization chamber. This work, as well as all the age measurements, were done at the Lamont Geological Observatory, Palisades, N.Y. The  $\text{Th}^{230}$  and  $\text{Pb}^{210}$  analyses

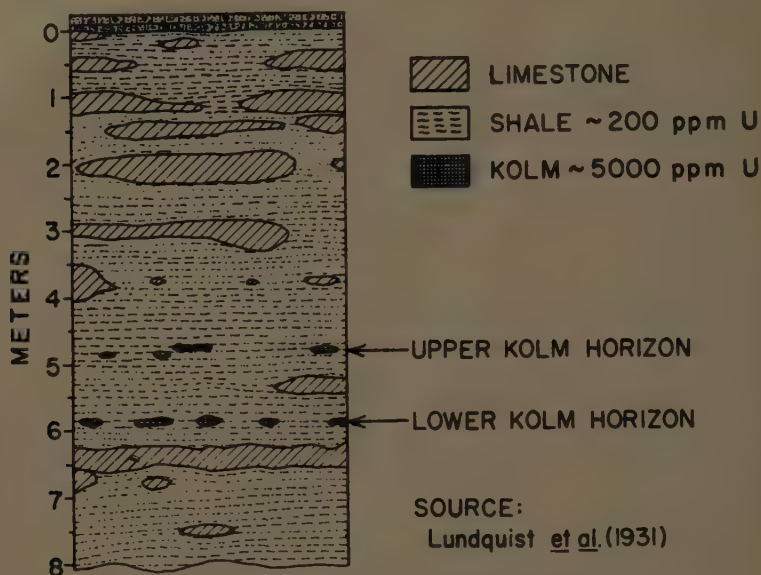


FIGURE 1. Sketch of Upper Cambrian shale near Stolan, Sweden.

TABLE 1  
APPARENT AGES ON SWEDISH KOLM AND SHALE

	U (ppm)	$(\text{U}^{238}/\text{Pb}^{206}) \times 10^6 \text{ yr.}$	$(\text{U}^{235}/\text{Pb}^{207}) \times 10^6 \text{ yr.}$	$(\text{Pb}^{207}/\text{Pb}^{206}) \times 10^6 \text{ yr.}$	$\text{Pb}^{207}/\text{Pb}^{206}$ ratio
<b>Kolm</b>					
S-14	5590 $\pm$ 120	360 $\pm$ 7	430 $\pm$ 10	865 $\pm$ 20	0.0675
S-15	5020 $\pm$ 80	355 $\pm$ 7	420 $\pm$ 8	840 $\pm$ 10	0.0667
S-24	6120 $\pm$ 60	400 $\pm$ 5	455 $\pm$ 10	800 $\pm$ 40	0.0655
S-25	5700 $\pm$ 85	225 $\pm$ 5	330 $\pm$ 8	920 $\pm$ 30	0.0693
S-19	6120 $\pm$ 60	380 $\pm$ 5	420 $\pm$ 10	720 $\pm$ 30	0.0631
<b>Shale</b>					
S-12	113 $\pm$ 2	550 $\pm$ 30			0.030 $\pm$ .012
S-17	306 $\pm$ 3	345 $\pm$ 15			0.055 $\pm$ .004
S-18	170 $\pm$ 1.2	530 $\pm$ 15			0.040 $\pm$ .010
S-20	317 $\pm$ 3	505 $\pm$ 15			0.056 $\pm$ .005

were done at Brookhaven National Laboratory.  $\text{Th}^{230}$  was determined directly by alpha counting using a pulse height analyzer coupled to a 100-channel analyzer. A known amount of  $\text{Th}^{228}$  was added to the sample to determine yield.  $\text{Pb}^{210}$  was measured by counting its  $\text{Po}^{210}$  daughter using the alpha-pulse height-analysis system. A known amount of  $\text{Po}^{209}$  was used as a tracer for this analysis. Errors were probably less than 5 per cent for the Th and Po measurements and were about 10 per cent for  $\text{Ra}^{226}$ .



The first Kolm lens depicted had isotopic ages representative of most Kolm analyses. The apparent isotopic ages are identical within the error.  $U^{238}$  and  $Th^{230}$  are in equilibrium, but  $Ra^{226}$  and  $Pb^{210}$  are not. There is a great difference in the  $Ra^{226}$  found in comparing the center and edge portions. This difference is not reflected in the  $U^{238}/Pb^{206}$  age. This means that this pattern is geologically recent. The  $Pb^{210}$  and  $Ra^{226}$  numbers are within analytical error but may indicate a uniform leaching of lead of a few per cent.

The next Kolm lens shown is the only one of four that showed any great difference in isotopic age. The 400 million year (m.y.) age on the center piece reflects loss of some uranium which occurred recently since the  $Th^{230}$  activity is high by 15 per cent. The very low 225 m.y. age of the edge piece must have been caused by recent movement of the lead isotopes, as evidenced by the low  $Pb^{210}$  activity.

TABLE 2  
COMPARISON OF ISOTOPIC AGE WITH PRESENT ALTERATION

	$(U^{238}/Pb^{206}) \times 10^6 \text{ yr.}$	Activity ratio: $U = 1.00$		
		$Th^{230}$ (80,000 yr.)	$Ra^{226}$ (1620 yr.)	$Pb^{210}$ (22 yr.)
Kolm lens 5.4 cm. thick				
center	360	0.995	0.82	0.736
edge	355	1.02	0.46	0.422
Kolm lens 6 cm. thick				
center	400	1.15	0.85	0.794
edge	225	0.995	0.68	0.370
Drill Core				
5.97 meters kolm	380	1.00	0.94	—
6.01 meters shale	345	1.01	1.0	0.830
5.21 meters shale	530	1.04	1.0	0.814

All these samples are from outcrops. The disequilibrium observed is due most probably, to ground-water leaching. Samples that have  $U^{238}/Pb^{206}$  ages of about 360 m.y. (the average  $U^{238}/Pb^{206}$  age) show  $Ra^{226}$  loss and loss of radiogenic lead. In the geological past, homogeneous extraction of these isotopes probably occurred continuously, although the extent of loss may have been different. Since the deposit has been at the surface, leaching has caused inhomogeneities in the isotopic ages by removing uranium and large amounts of lead in some isolated cases.

The samples in the drill core show less disequilibrium and no apparent correspondence with the isotopic ages. Whatever caused these apparent ages must have occurred in the geological past.

On the basis of the explanation that  $Ra^{226}$ ,  $Pb^{206}$ , and  $Pb^{207}$  loss have been dominant in causing the highly discordant pattern exhibited by the Kolm samples, it is possible to arrive at a conclusion as to the minimum age for this Upper Cambrian formation. This may be seen graphically in FIGURE 2.

This is a plot of  $Pb^{206}/U^{238}$  versus  $Pb^{207}/Pb^{206}$ . The heavy line is the concordia line for this diagram. The insert shows what happens to samples originally on the line that have been subjected to lead loss, uranium loss, and loss of



$Ra^{226}$ . The points representing Kolm samples spread out in a direction clearly indicative of  $Ra^{226}$  loss.

The scatter of points from the line represent various amounts of lead loss. The line drawn through the uppermost Kolm points and intersecting concordia

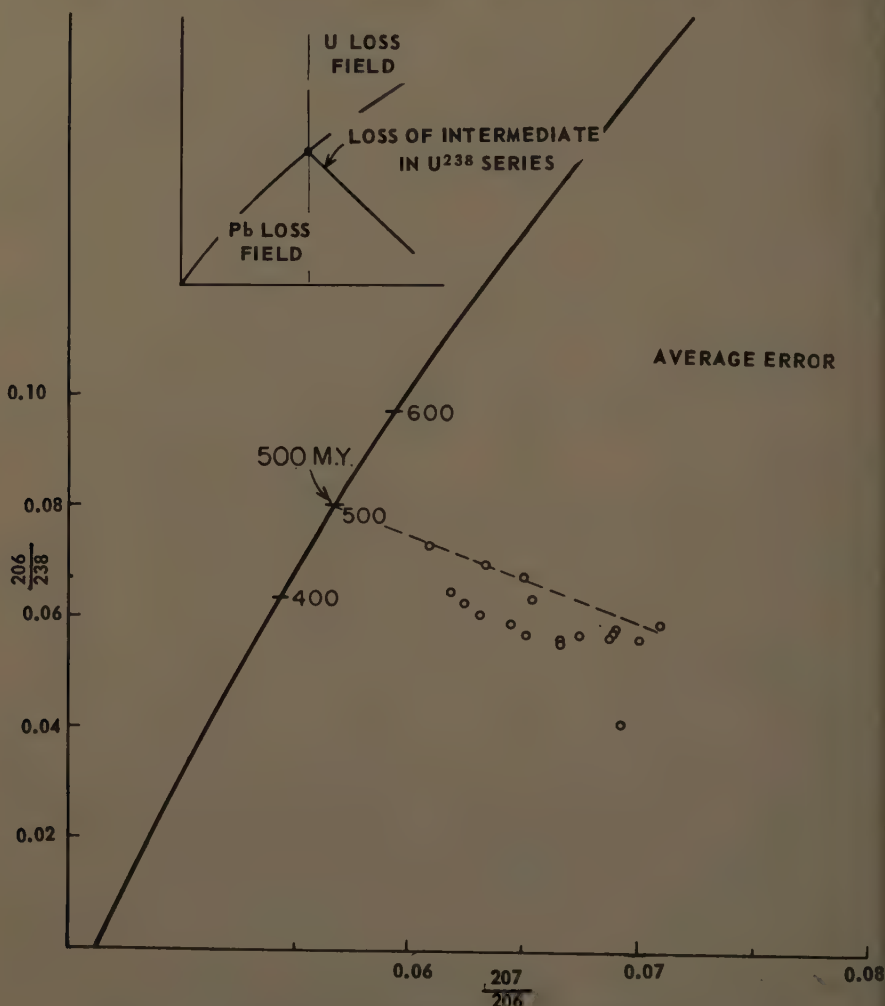


FIGURE 2. Plot of  $Pb^{206}/U^{238}$  versus  $Pb^{207}/Pb^{206}$  for Swedish Kolm samples.

at 500 m.y. gives a minimum age for the formation. The distribution of points suggests that  $Ra^{226}$  loss has been dominant over lead loss, just as is found at the present time. The effect of  $Ra^{226}$  loss from the Kolm is emphasized when the shale points are plotted on a  $Pb^{206}/U^{238}$  versus  $Pb^{207}/Pb^{206}$  diagram (FIGURE 3). Here, it can be seen that  $Ra^{226}$  from the Kolm has been deposited in the shale, resulting in anomalously high  $Pb^{206}$  concentrations. Loss of  $Pb^{206}$  and  $Pb^{207}$  by leaching has caused the scatter in the shale points.

Uranium-lead dating has also been attempted on the Upper Devonian Chattanooga shale. TABLE 3 presents the data obtained. The most uraniferous horizon, from which these samples were taken, is about four feet thick. The values obtained on the daughter product activity are encouraging. Perhaps

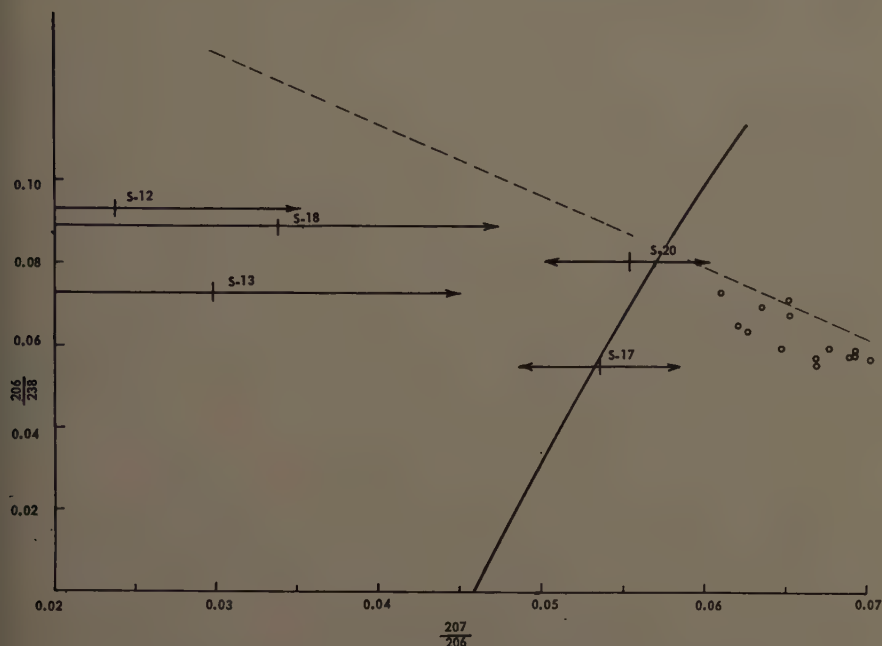


FIGURE 3. Plot of  $Pb^{206}/U^{238}$  versus  $Pb^{207}/Pb^{206}$  for Swedish shales.

TABLE 3  
CHATTANOOGA SHALE AGES  
Drill Core YB-9

U(ppm)	$U^{238}/Pb^{206}$ age $\times 10^4$ yr.	Activity ratio: $U = 1.00$		
		$Th^{230}$ (80,000 yr.)	$Ra^{226}$ (1620 yr.)	$Pb^{210}$ (22 yr.)
$90.6 \pm 0.9$	$350 \pm 15$	$0.98 \pm 0.1$	—	$1.0 \pm .05$
$68.3 \pm 0.7$	$350 \pm 15$	$1.05 \pm 0.1$	$1.1 \pm 0.1$	$0.98 \pm .04$

samples taken from deep drill cores are more stable to leaching than surface deposits like the Swedish alum shale.

It should be noted that this formation is both lower in uranium and younger in age than the previous example. This emphasizes a problem that has not been discussed so far: the correction for nonradiogenic  $Pb^{206}$ . The error quoted on the 350 m.y. age is simply error in the chemical analysis. The isotopic composition of the lead used for the correction was a model common lead of Devonian age. Another choice of lead is illustrated in FIGURE 4. Here  $U/Pb$

is plotted against  $Pb^{208}/Pb^{206}$ . Two of these samples were shown on the previous slide. The other two are from neighboring horizons with lower uranium contents. The intersection differs from the model  $Pb^{208}/Pb^{206}$  value by 4 per cent. This in itself is not a great error but, in view of the low U/Pb of the rock, this causes about a 12 per cent error in the  $U^{238}$ - $Pb^{206}$  age. Therefore, the apparent age of the formation lies somewhere between 320 and 350 m.y.

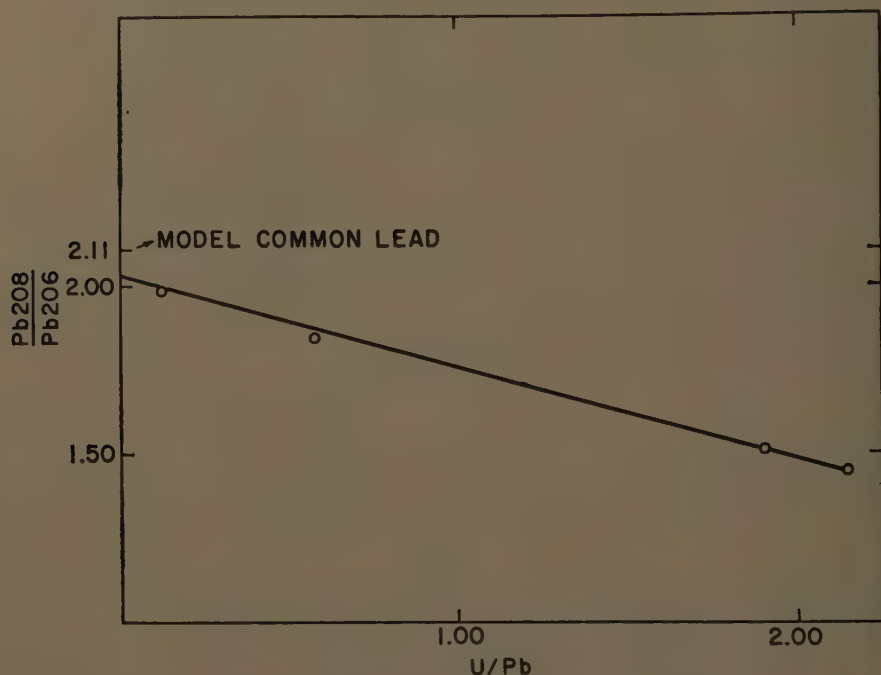


FIGURE 4. U/Pb ratios on Chattanooga, Tenn., samples.

Reviewing the possibilities and problems of U-Pb dating on black shales, the following conclusions can be drawn:

- (1) The principal cause of discordant U-Pb ages is ground-water leaching. Radium and lead are most susceptible to this effect. Deep samples from drill cores are likely to show less leaching effects than surface samples.
- (2) If only  $U^{238}/Pb^{206}$  ages can be obtained, they are probably minimum. If the horizon is high enough in uranium to calculate three isotopic ages, this can be of assistance in determining what has happened.
- (3) Younger samples than Paleozoic would be very difficult to use because of the high common lead correction required.

## DATING OF TERTIARY VOLCANIC ROCKS BY THE POTASSIUM-ARGON METHOD\*

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Judging by the present widespread use of the K-Ar method of dating, it might be supposed that such researches have been going on for a long time. Actually, however, 12 years ago it was shown that argon-40 is the decay product of potassium-40. At this time it was suggested that, since potassium does electron-capture to produce argon-40, potassium possibly might be important in geological dating. The applications since that time have been widespread and important, as a survey of the literature will attest.

This paper will report in a preliminary way some results on the possibility of using volcanic glasses for K-Ar dating. In order to be useful for K-Ar dating, a mineral should have the following characteristics: (1) it should be relatively widespread in natural settings; (2) it should be completely outgassed of argon at the time of the geological event it is to mark; (3) it should undergo little loss of argon by diffusion; and (4) it should contain a reasonable amount of potassium.

The instrument used in the present investigation is a metal mass spectrometer with glass ends that has been adapted for static operation. The detector employed a vibrating reed electrometer with a  $10^{11}$  ohm input resistor. With this arrangement  $10^{-10}$  standard cc. of argon is easily measurable. The apparatus is well suited for dating tertiary rocks; however it is awkward to attempt dating a rock that is a billion years old since only a milligram or so of sample can be used without flooding the mass spectrometer with argon.

The mass spectrometer has, as an integral part, a sample-handling system so designed that the amount of contamination from air argon will be minimized. The procedure consists of melting the sample, purifying the argon by adsorption and desorption on charcoal, and by contacting with titanium metal at  $800^{\circ}$  C. The purified argon is added directly to the mass spectrometer that is then operated under static vacuum conditions.

The potassium was determined gravimetrically using sodium tetraphenylboron as the precipitant.

In the course of the determination of young ages, it was found that the argon-38 standard available had an uncomfortably large amount of argon-36 in it. As a result, a sample of argon-38 was prepared by irradiating spectroscopic grade potassium chloride with neutrons at the Brookhaven reactor. The isotopic analysis for those isotopes of interest in potassium-argon dating is shown in TABLE 1. Argon-39 is not included but corresponds to about 3 per cent.

The lava samples used in the present investigation were collected by Paul

\* The work reported in this paper was supported in part by the United States Atomic Energy Commission, Washington, D.C.

Argon 38 standard of composition similar to that used in this investigation may be obtained through Louis Stang, Brookhaven National Laboratory, Upton, N.Y.

Kerr of Columbia University, New York, N.Y., and his students. Geological interpretation of the results will be presented elsewhere at a later date.

To determine if volcanic glasses at the time of solidification are completely outgassed, a very young specimen, supposedly Pleistocene, was chosen for analysis. If there were any residual argon-40, the resulting error would be greatly magnified for a young glass such as this. The results, using the constant 3.7% K, sample weight 10.9 gm., are as follows: K-Ar age 1.5 m.y.; 54 per cent radiogenic Ar<sup>40</sup>. Of particular interest is the fact that 54 per cent of the total argon recovered was found to be radiogenic in origin. From the calculated age of 1.5 m.y. it is evident that lavas are apparently outgassed at the time of cooling; at most, an error corresponding to a million years could be introduced

TABLE 1  
ARGON-38 PREPARED AT BROOKHAVEN NATIONAL LABORATORY

	Per cent
Ar <sup>38</sup>	95.3
Ar <sup>40</sup>	1.68
Ar <sup>36</sup>	0.015

TABLE 2  
POTASSIUM-ARGON AGE OF MARYSVALE, UTAH, LAVAS IN 10<sup>6</sup> YEARS

KA-28	KA-29	KA-14	KA-11 (biotite)
19.5	25	22	25
14.2	18	14	22
25.5	13	20	27
19.0	24	20	20
19.0	20	20	25
		20	24
		18.4	
19.3	19.9	19.1	23.7 Average K-Ar age

from this source. Efforts are being made to obtain a more recent sample to pursue this point further.

TABLE 2 contains the results from some lava samples from the Marysvale, Utah, area. All of these samples are stratigraphically of the same age. The data for the three glass samples represent 1-gm. portions taken from massive glass specimens. All data, even that from the early developmental phase of the investigation, have been included, resulting in a considerable spread in the observed ages. It may be seen that the biotite in this series, which should be roughly of the same age, shows only a slightly higher age than the glass samples, indicating that the diffusion loss of argon from these samples was not very serious.

TABLE 3 shows the results for a glass and a biotite taken from the same rock. In this case, in contrast to the samples of TABLE 2, the glass was fine grained and had to be picked out by hand with the aid of a microscope. There is a



definite difference in the observed ages of the glass and the biotite; it would appear that this particular glass had lost about one half of its argon in only 20 m.y.

It may be concluded on the basis of these rather preliminary measurements that volcanic glasses have a good possibility of being a useful mineral for K-Ar dating, provided that samples for analysis are taken only from fairly large specimens.

### *Discussion of the Paper*

L. F. HERZOG (*The Pennsylvania State University, University Park, Pa.*): How radioactive is the argon? How much  $\text{Ar}^{39}$  is present in this spike?

SCHAEFFER: It has  $\text{Ar}^{39}$  in the microcurie level.

P. E. DAMON (*University of Arizona, Tucson, Ariz.*): I wonder if there is any possibility that the second volcanic glass (KA-12) is devitrified. In this age range such glasses commonly are devitrified.

BASSETT: Yes, I think there may be a possibility that it is devitrified. We have not had a look at it under the microscope, which is one thing I intend to do,

TABLE 3  
POTASSIUM-ARGON AGE OF MARYSVALE, UTAH, LAVAS IN  $10^6$  YEARS

	Glass	Biotite
KA-12	15	22
	11.5	26
		27
Average K-Ar age	13 m.y.	25 m.y.

but it looks lighter in color and has a somewhat milky appearance that might indicate that it is devitrified.

G. H. CURTIS (*University of California, Berkeley, Calif.*): We have dated a number of glasses, or at least we have attempted to, starting when J. Lipson was with us several years ago, and we have found very good concordance with biotite or sanidine ages in some and very poor concordance in others. In all cases, the poor ones were devitrified. Sometimes this is very difficult to see. Devitrification is so imperceptible, the grains are so small that they cannot be seen, but they do show up under high power and if the specimen is crushed.

The unfortunate thing about glass, except in the case of welded tuffs, is that it is usually in the form of very fine fragments or ash deposits, and these are, except under very favorable conditions, nearly always devitrified.

We have found them as old as Lower Miocene under conditions in which devitrification might be expected but in which they were fresh and gave concordant ages with sanidine. Thus all geologists should keep in mind that glasses can possibly give useful dates, but that a 50 per cent mortality can be expected even on good-looking material.

G. J. WASSERBURG (*California Institute of Technology, Pasadena, Calif.*): I wonder if the observations of Clarence Ross of the United States Geological

Survey on the hydration of volcanic glasses have any bearing on your work. He has suggested that much of the water in volcanic glasses was taken up subsequent to the extrusion of the lava. Is the water content in any way related to the retentivity?

BASSETT: This hydration proceeds on a front that advances into the grain in time and flakes off the outer layers due to the accumulating tensions. The hydration is not uniform. It proceeds from the outside and it is impossible to get rid of this layer even if desired.

G. W. WETHERILL (*Carnegie Institution of Washington, Washington, D.C.*): No. However the point is that these are still glasses, and the fact that they are not devitrified, may explain why they have low values.

BASSETT: The first glass samples certainly showed no indication of being very hydrated. They are far from being pearlite, and there is no indication during the fusion that there is an excess of water in these.

WETHERILL: Could you tell me how much normal argon contamination is encountered?

SCHAEFFER: These samples all ran more than 50 per cent radiogenic argon, which corresponded to a contamination level of about  $10^{-7}$  cc. at NTP.

To get a low blank one must keep the apparatus hot for hours to get the argon out of the walls. We use charcoal to move the argon around. Using just a few grains of charcoal and keeping everything else as small as possible helps to keep the argon contamination low.

S. R. HART (*Massachusetts Institute of Technology, Cambridge, Mass.*): Do you use any sort of outgassing for the sample?

SCHAEFFER: Yes. We have tried several sorts of experiments. We normally load 5 to 12 samples into the sample line at once and then run them successively without opening up again. We have baked them at various temperatures and collected the gas in order to see how much radiogenic  $\text{Ar}^{40}$  is released. We found that if we heat at  $500^{\circ}\text{C}$ . appreciable radiogenic  $\text{Ar}^{40}$  is observed. We usually bake samples overnight at a temperature of between  $100^{\circ}$  and  $200^{\circ}\text{C}$ . We do not lose any radiogenic  $\text{Ar}^{40}$  by that procedure, but it greatly reduces the amount of air argon that is in the determination. A good part of the natural abundance argon contamination after preliminary baking comes from the interior of the rock itself.

DAMON: I wonder if there is some virtue in using argon-39 as a tracer?

SCHAEFFER: Whatever isotope, 38, 39, or 37, is used to monitor, it is the peak at 36 that makes the trouble. In the Oak Ridge samples of  $\text{Ar}^{38}$ , it is not that they do not have enough 38 in them: it is that they have too much 36.

## POTASSIUM-ARGON DATES ON BASALTIC ROCKS\*

G. P. Erickson and J. Laurence Kulp

*Lamont Geological Observatory, Columbia University, Palisades, N.Y.*

Although basalt is one of the most common rocks of the earth's crust it has not been generally useful for geological dating by radioactive methods. The U/He method was investigated by Hurley (1941, 1943) and by Keevil (1942) who found that such large losses of helium had occurred from whole rock and from several mineral separates that the method could not be dependably applied. In the case of the Rb/Sr method, the high common strontium content of basalts so greatly reduces the accuracy of the method that it is practically useless. Work with potassium and argon has been largely discouraged by the uncertain argon retentivity of the rock as a whole and of the constituent minerals and also because of the low potassium concentration that makes analysis difficult for both potassium and for the resultant argon. However, recent developments in argon mass spectrometry have made possible a systematic investigation of the applicability of the K-Ar method to basalts. Such a study is in progress at the Lamont Geological Observatory, and we shall present a brief preliminary report on some of the data.

The Palisades Diabase sill and its related basalt flows were chosen as the geological units for this study for several reasons. The differentiation of the sill has resulted in a number of different petrological phases and types including contact metamorphic rocks. Also, locally there is sufficient biotite present to be removed and run separately. The comparatively well-known argon retention characteristics of biotite provide a valuable reference for the other parts of the rock. In addition, this unit is stratigraphically quite well located in the Upper Triassic, and the biotite data provide a means of calibrating the paleontological time scale in this region.

In TABLE 1 it is seen that the biotite separated from the diabase gives an apparent age of  $190 \pm 5$  million years (m.y.). Since there has been no significant reheating evident in the geological history of this unit, this may be the age of the intrusion of the sill. It is commonly considered that the Watchung basalt lavas belong to the same general period of activity; thus, this may be the age also of the neighboring sediments.

The other samples are all of whole rock, and it is apparent that the argon retentivity of certain phases of the diabase is comparable to that of biotite. The chilled phase at the contact between the sill and the enclosing sediments has the highest retentivity, giving an apparent age slightly higher than that of the biotite but having much larger uncertainty. Toward the interior of the sill the rock is coarser in texture and has retained somewhat less of its argon. The ages indicated in the table are of interest only in reference to the biotite that for this comparison is assumed to have retained all of its argon.

The fine-textured diabase has plagioclase laths approximately a few tenths of 1 mm. in length, while the plagioclase in the coarser diabase has an average length of several millimeters.

\* Lamont Geological Observatory Contribution No. 463.

It is probable that these variations in retentivity are only indirectly related to texture. In thin section the coarser, later crystallizing rock shows evidence of somewhat more secondary alteration than the fine rock, and it also has more potassium feldspar as a distinct mineral, as well as other mineralogical differences. It is generally accepted that potassium feldspar may lose a large part of its radiogenic argon and, in this case, this may contribute significantly to the total loss from the rock.

The baked shale from below the Palisades sill was analyzed, and the whole rock shows a very high retentivity. In addition, one very fine textured sample from the Watchung basalt was run, and that shows a retentivity of only 40 per cent, assuming that it has the same age as the biotite sample from the diabase.

A geologically interesting area where this method may provide some valuable data not otherwise available is the ocean floor. One sample dredged from the

TABLE 1

POTASSIUM-ARGON MEASUREMENTS ON THE PALISADES DIABASE AND WATCHUNG BASALT

Sample	K(%)	Apparent age (m.y.)	Retentivity (%)
Palisades Diabase			
Biotite	6.41*	190 $\pm$ 5	
Whole rock at contact	0.52	202 $\pm$ 10	~100
Fine	0.61	202	~100
Medium (above center of sill)	0.73	166	~85
Medium (below center of sill)	0.55	142	~75
Coarse	0.89	162	~85
Hornfels below sill			
Whole rock	1.80	193	~100
Watchung basalt			
Whole rock	0.19	79	~40

\* Ledoux and Company, Teaneck, N.J.

mid-Atlantic Ridge by Ewing was run and, assuming a reasonably high retentivity, an age for this sample of less than 5 m.y. was obtained. Actually no radiogenic argon at all was found in this rock, but a conservative estimate of the uncertainties involved, chiefly due to the large amount of atmospheric argon present, results in this 5 m.y. outside limit. This confirms that there has been volcanic activity in this portion of the ocean floor in recent geological time.

All of these argon analyses were made by the standard isotope dilution technique, using a high sensitivity Reynold's type mass spectrometer. The potassium analysis of the biotite was done by flame photometry at a commercial laboratory.\* The others, including the surprisingly low potassium concentration of the Watchung basalt, 0.19 per cent, were done by isotope dilution and solid source mass spectrometry. In this range of potassium concentration we have not found flame photometry to be a very reliable method of analysis. The potassium analysis for the mid-Atlantic Ridge basalt was made by Paul

\* Ledoux and Company, Teaneck, N.J.

Gast some time ago, using isotope dilution on another piece of the same rock that was used for the argon determination.

Evidently more work is required before this method can be applied with confidence to basalts more generally. We hope to determine the location of the potassium in this rock and, from that study, to provide better control on the retentivity. The present data, however, looks very promising.

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### *Discussion of the Paper*

P. E. DAMON (*University of Arizona, Tucson, Ariz.*): Some years ago P. M. Hurley made a study of the Palisades Diabase using the helium method, and I am curious to know from him just how this compares with the recent argon work.

P. M. HURLEY (*Massachusetts Institute of Technology, Cambridge, Mass.*): My associates and I separated a sample into mineral fractions and found that the feldspar showed a retentivity of about 20 per cent and the mafic constituents exclusive of the glass showed a retentivity of about 70 per cent. This retentivity figure was determined against a value obtained for magnetite from Triassic intrusives in Pennsylvania, which showed an age of about 170 m.y. We assumed the magnetite to be 100 per cent retentive from quite a number of other measurements that were compared with the existing lead time scale.

B. J. GILETTI (*Oxford University, Oxford, England*): How does this boulder relate to the one that was reported by Carr and Kulp, using the helium method? Is it the same one?

ERICKSON: This is a piece of the same boulder. The result they reported was  $30 \pm 15$  m.y., but that was done by the total helium method and alpha counting. They claimed only that it demonstrated volcanic activity in Cenozoic time. This result should be considered a refinement.



# THE POSSIBILITY OF UTILIZING THE ABSOLUTE AGE OF METAMORPHIC AND FRAGMENTAL ROCKS IN PALEOGEOGRAPHY AND PALEOTECTONICS

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At the present time, radioactive methods are widely used in geology to determine absolute ages. However work in this area has chiefly been concerned with determinations of the time of formation of intrusions and veins. Recently a number of publications have appeared on the age of effusive rocks and sedimentary minerals (glauconites). In these cases the problem is to determine the time of deposition of sedimentary rocks or the time of formation of effusive rocks.

Nevertheless the range of application of radioactive methods of age determination in geology can be extended still further. The argon method is particularly suitable in this respect; its advantage lies in the facts that potassium-containing minerals are widely distributed and that radiogenic argon is largely retained in these minerals.

In this paper, I shall show the desirability of applying the argon method to metamorphic and terrigenous sedimentary rocks in order to extend the application of this method in paleogeographic and paleotectonic reconstructions. Using as examples the central portion of the northern zone of the Tien Shan (which my associates and I have studied and which is of a uniform geological age) and certain other regions, I propose to:

- (1) Discuss the ages of rocks formed in the principal magmatic cycles of the central Tien Shan;
- (2) Discuss the possibility of determining the time of metamorphism of metamorphic rocks;
- (3) Trace the changes in the K/Ar ratio that accompany weathering of granites;
- (4) Discuss the extent to which radiogenic argon and potassium are retained in granite boulders, arkosic sand, sandstones, clays, and silts;
- (5) Discuss the loss of argon from feldspars in relation to their structural features; and
- (6) Illustrate the use of the method in paleogeographic reconstructions.

This is a wide circle of different problems, any of which is a suitable subject for special investigation. I cannot answer any of these questions exhaustively in this article but have purposely combined them in order to show, using studies of a single region as an example, the enormous possibilities of applying the argon method directly to rocks and the diversity of the questions that can be answered thereby. It is possible by means of this approach to demonstrate several new directions the use of this method might take and to indicate that the interrelations and mutual connections of these applications can be convincingly shown only by such a simultaneous examination of these problems.

## *Ages of Magmatic Rocks of the Central Tien Shan*

Since relatively constant values are obtained for granitoids of the same geological age, it is possible to classify various granitoid complexes with con-

fidence (within the limits of the precision indicated).<sup>11-13</sup> Comparatively constant values obtained also for effusive rocks,<sup>16</sup> although these have been studied less extensively than intrusive rocks.

TABLE 1 shows the ages of the principal cycles and phases of magmatic rocks of the Central Tien Shan. The ages were obtained by direct determinations on these rocks by the argon method. The accuracy of the mean values cited here is somewhat better than usual as a result of painstaking verification and compensation for errors.

On the whole, the values obtained for these ages are in agreement with geologic concepts. The "Salair" cycle, which we have conditionally differentiated, is conditional with respect to: (1) the accuracy of the age determination (these rocks were altered somewhat), and (2) its geological justification (granitoids in the metamorphic rocks). It should be noted that the Tertiary age of

TABLE 1\*

No.	Tectonic-magmatic cycle and phase	Number of samples	Age (m.y.)	Geologic age		
				From geologic observations	Holmes's scale 1947	Scale of Mayne <i>et al.</i>
1	<i>Salair</i> $\gamma_1$	5	525	Pre-Cm(?)	Cm-Pr	S
2	<i>Caledonian</i>					
	Effusive rocks $\delta_2$	5	385	0	0	C <sub>1</sub>
	Basic rocks $\gamma_2^1$	3	370	0	0	C <sub>1</sub>
	Porphyroid granites $\gamma_2^2$	23	370	0	0	C <sub>1</sub>
	Alaskite granites $\gamma_2^3$	21	355	0	S-0	C <sub>2</sub>
3	<i>Hercynian</i>					
	Effusive rocks $\delta_3^1$	5	290	D(?)	D	P <sub>1</sub>
	Effusive rocks $\delta_3^2$	10	280	C <sub>1</sub>	D	P <sub>1</sub>
	Syenites $\gamma_3^1$	5	280	P-C	D	P <sub>1</sub>
	Granites $\gamma_3^2$	8	270	P-C	D	P <sub>1</sub>
4	<i>Alpine</i>					
	Basalt $\delta_4$	3	55	Pg	Pg	Pg

\* In calculating ages, the following constants have been employed:  $\lambda_\alpha = 5.57 \times 10^{-11} \text{ yr.}^{-1}$  and  $\lambda_\beta = 4.72 \times 10^{-10} \text{ yr.}^{-1}$ .

basalts lying at the bottom of the red-colored stratum proves conclusively that this entire stratum in the northern zone of the Tien Shan should be assigned a Tertiary age (some investigators believe it is made up of Cretaceous deposits).

In TABLE 1 is presented a comparison of geologic data with the ages obtained as they are represented on different scales. For rocks of Hercynian age better agreement is obtained with the new scale of Mayne *et al.*<sup>20</sup> Reduction of the ages on the old scale of Holmes in this interval has also been noted previously by many Soviet investigators. For Caledonian formations, the Holmes scale fits better.

At this point a word should be said about the "absoluteness" of the ages in TABLE 1. On the basis of general considerations concerning the reduction of ages determined from feldspars and judging from indirect data of comparison with certain vein minerals, it can be granted that the absolute ages of these rocks are somewhat low. The age of the Caledonian granitoids is possibly around 420 m.y. and that of the Hercynian granitoids about 320 m.y. How-

ever, since our chief purpose is to study the age relationships of various rocks and their disintegration products as determined by the argon method, in the discussion that follows we will use the data given in TABLE 1. It should also be mentioned that our values for the main intrusive phases (Caledonian, 370 to 420 m. y. and Hercynian, 270 to 320 m. y.) have been confirmed for other regions of the U.S.S.R. and agree with the old data of Walter Wall.

TABLE 2

No.	Site	Rock	K(%)	Ar( $\frac{\text{cm}^3}{\text{gm.}} \times 10^{-6}$ )	Age (m.y.)
<i>Proterozoic rocks</i>					
1		Muscovite gneiss	2.58	5.04	455
2		Muscovite gneiss	2.81	5.06	420
3		Feldspar-muscovite gneiss	2.85	5.38	445
4		Biotite gneiss	1.67	2.87	405
5		Feldspar-muscovite gneiss	2.10	3.14	360
6		Feldspar gneiss	2.44	3.76	370
7		Feldspar gneiss	3.04	4.55	360
8		Amphibolic schist	0.71	0.94	320
9	Kurday	Feldspar-biotite gneiss	1.26	2.21	415
10	Ottuk	Feldspar-biotite gneiss	1.48	2.44	390
11	Ottuk	Feldspar-biotite gneiss	3.11	5.17	395
12	Ottuk	Biotite gneiss	3.70	5.61	360
<i>Lower Paleozoic rocks</i>					
13	Terskey Ala-Tau Ridge	Composite sample	2.00	3.44	405
14	NW part of Ala-Tau Ridge	Composite sample	1.65	2.49	360
15	Dzhety-Oguz	Biotite gneiss	2.09	3.31	375
16	Dzhety-Oguz	Biotite gneiss	1.52	2.48	385
17	Dzhety-Oguz	Feldspar-biotite gneiss	3.60	5.94	390
18	Dzhuuka	Quartz-biotite hornfels	3.07	4.67	365
19	Dzhuuka	Sericite-chlorite schist	4.03	6.62	390
20	Barskaun	Chlorite schist	1.57	2.46	375
21	Barskaun	Chlorite schist	3.57	5.65	375
22	Barskaun	Chlorite schist	2.71	4.45	390
23	Barskaun	Chlorite schist	4.34	7.51	410
24	Sary-Bulak	Calcareous-micaceous schist	1.83	2.62	345
25	Sary-Bulak	Micaceous schist	3.29	4.64	340
26	Sary-Bulak	Hornfels	3.10	5.45	415
27	Kil'densu	Micaceous schist	2.39	3.64	365
28	Minkush	Micaceous schist	2.60	4.04	370
29	Minkush	Feldspar-biotite gneiss	4.71	6.98	355
30	Achik-Tash	Feldspar-biotite gneiss	3.98	6.43	385

*The Argon: Potassium Ratio in Metamorphic Rocks of the Northern Zone of the Tien Shan*

When we determine the age of a rock by the argon method, we determine the time of crystallization of potassium-containing mineral. Accordingly, for metamorphic rocks this is the time of recrystallization, primarily of micas and feldspars. If metamorphism of the rock was complete and encompasses a fairly large area, then upon applying the argon method of age determination to these rocks we ought to obtain rather uniform values corresponding to the time of metamorphism of the stratum in question.<sup>11,14</sup> As an example, let us consider the metamorphic rocks of the northern zone of the Tien Shan (TABLE 2).

In the region investigated, we observed three distinct intrusive cycles with

ages (by the argon method applied to the granites) of 525, 370, and 280 m. y. In addition, Alpine orogeny was intensively displayed, and there were also a number of less distinct movements of the earth's crust.

However when did the ancient deposits undergo metamorphism to such an extent that they assumed their present form? When did gneisses become gneisses, and schists become schists? Was this a single process in time and space?

To lay the groundwork for answers to these questions we selected for study a fairly extensive region of the northern zone of the Tien Shan. The principal stage of metamorphism here is naturally connected with the Caledonian epoch of intrusive activity, when the geosynclinal phase of this region's development had practically come to an end. Nevertheless the roles played by earlier and later epochs of folding in metamorphism of the sedimentary rocks are not altogether clear.

An examination of the results, presented in the table, of age determinations of metamorphic rocks leads to the following conclusions.

(1) For the great majority of the metamorphic rocks analyzed from the northern zone of the Tien Shan, an age close to that of the Caledonian granitoids (350 to 400 m. y.) was obtained.

(2) The ancient Proterozoic rocks (they may also be Archean) of the Tien Shan complex were metamorphosed (into gneisses) in the Caledonian epoch. The somewhat greater age of the muscovite gneisses is explained by the usual 15 to 20 per cent elevation of "muscovite" age over "feldspar" age. It follows that all these gneisses are of the same age. The majority of the Lower Paleozoic rocks were metamorphosed during the Caledonian epoch into schists and, in contact zones, into hornfels.

(3) Later tectonic movements did not result in any substantial recrystallization of rocks.

(4) As a general conclusion, we may note that studies by the argon method of the time of the principal (most recent) metamorphism of sedimentary rocks (and in the case of recrystallization, probably also effusive rocks) yield quite constant results; consequently, this method may be used to determine the "level of metamorphism in time" of a given region of the earth's crust.

#### *Use of the Argon Method to Answer Paleotectonic Questions*

The constancy of the ages of metamorphic rocks of given tectonic zones, which we have indicated above and have previously described in somewhat greater detail<sup>11,13,14</sup> is of fundamental importance and allows us to extend the application of the argon method to answer a number of paleotectonic questions. The argon method is well suited to determining whether tectonic-magmatic processes occurred at the same time. It may be used also to compare nonadjacent portions of tectonic-magmatic zones and show parallels between them. We have given a partial demonstration of this using the Antarctic as an example (elsewhere in this monograph).

Quite a number of other examples could be cited. Contemporaneous tectonic-magmatic zones are now beginning to appear in a limited number of analyses of metamorphic rocks from the Russian Platform (the Urals, Taymyr,



and Central Asia). It is not possible for us to discuss these examples in greater detail in the present article but, in general, application of the argon method to metamorphic and intrusive rocks permits us to identify relics and contours of ancient tectonic-magmatic zones. It can thus give a measure not only of the time when individual tectonic processes occurred but also—to some extent—of the intensity of those processes.

*Changes in the Argon:Potassium Ratio Accompanying Decomposition of Granites and Transportation of the Decomposition Products*

Since minerals naturally lose part of their potassium and argon as a result of weathering, the question arises as to the stability of the ratio  $\text{Ar}^{40}/\text{K}^{40}$  at various stages of weathering and transportation of the decomposition products of rocks and minerals.

TABLE 3

DECOMPOSITION OF GRANITE ("DELUVIAL" TYPE\* OF WEATHERING, LONG-DISTANCE TRANSPORT BY RIVERS, AND WEATHERING BY LAKE SURF)

No.	Rock	Particle size (mm.)	K(%)	Ar( $\frac{\text{cm.}^3}{\text{gm.}} \times 10^{-5}$ )	T (m.y.)
1	Granite (monolith)	—	3.01	4.82	380
2	Granite (monolith)	—	3.43	5.09	355
3	Strongly weathered granite	—	3.56	4.94	335
4	"Deluvium"* (gravel)	1-5	3.0	3.08	250
		(Trans: 10-50?)	2.91		
5	"Deluvium"* (sand)	3-10	2.43	3.15	265
6	"Deluvium"* (fine sand)	0.3-0.5	2.78	3.34	330
7	River sand	0.3-0.5	2.40	4.24	365
8	River pebbles	4-8	3.51	3.85	380
9	Lake sand (at river mouth)	1-2	2.83	5.29	360
10	Lake sand (at river mouth)	1	4.43	4.72	395
11	Lake pebbles	5-8		7.52	400
12	Delta clay	0.01	2.98	4.11	335

\* Deluvium = debris transported down mountainsides by gravity, rain, or snow.

Let us consider the disintegration of gray porphyroid Caledonian granites of the Tien Shan (TABLE 3). Samples were taken from the valley of the Barskaun River, a tributary of Lake Issyk-Kul'. This river cuts through Caledonian granites; we can therefore say with confidence that we are tracing various stages in the transportation of the same rocks.

When traces of weathering are distinct, the granite loses approximately 10 per cent of its argon. Pieces of granite carried down the mountainsides, which represent fragments of strongly eroded granite, have lost from 10 to 30 per cent of their argon. Characteristically, the loss of argon is greatest in the biggest fractions of this type of debris.

Sands and pebbles from rivers and lakes have the same argon:potassium ratio as unchanged granites. In fact, in the lake varieties the ratio is even somewhat higher. This pattern can be explained by natural selection. Material that was soft and unstable at the previous ("deluvial") stage of erosion was eliminated during rough treatment by river currents and lakeshore surf;



the more stable material remained. It should be noted that Sample 12 contains delta clay; its age was also approximately equal to that of the original granite.

What transformations occurred in the relatively unstable portions of the crystals that showed reduced ages in the initial stages of weathering? Neither the large nor the finest products of the ultimate disintegration of these granites displayed reduced ages. It would appear that, as a result of the loss of argon, potassium was also lost. These portions of the crystals were probably dissolved to a large extent.

Unfortunately, space does not permit us to cite here a number of other interesting instances of changes in the argon:potassium ratio. Some examples are discussed in another paper of ours.<sup>15</sup> We shall mention only that, in other types of weathering as well, the argon:potassium ratio is commonly reduced 10 to 30 per cent during the initial stages of rock decomposition and, in the final products of decomposition, again returns to the level observed in fresh

TABLE 4  
GRAY PORPHYRITIC GRANITES (370 M.Y.)

No.	Size (cm.)	Type of deposit	Site	K(%)	Ar ( $\frac{\text{cm.}^3}{\text{gm.}} \times 10^{-8}$ )	T (m.y.)
1	3-6	Lake	Tossor	3.80	6.18	385
2	4-8	River	Barskaun	2.40	3.85	380
3	3-8	River	Tossor	3.21	4.62	345
4	20	Glacial	Barskaun	3.86	6.17	380
5	50	Glacial	Dzhergalan	3.73	5.73	370
6	30	Glacial	Dzhergalan	3.64	4.93	330
7	5-10	Conglomerate Q	Barskaun	3.03	4.46	355
8	1-3	Conglomerate Tr	Dzhety-Oguz	3.18	4.52	340
9	5	Conglomerate C	Chu	1.38	2.23	385

rocks. The ratio does not change significantly unless distinct chemical changes occur in the rock, with complete alteration of its potassium-containing minerals.

#### *Dating of Pebbles, Sands, and Sandstones*

In the preceding section it was shown that, in the terminal decomposition products of granitoids, the argon:potassium ratio remains the same as in the original fresh rocks. If this is so, then we can evidently determine the age of the mother rocks from pebbles and arkosic sands<sup>9</sup> and can also apply the argon method to sandstones in order to answer paleogeographic questions.<sup>11,15</sup> We shall present a few examples from materials from the Central Tien Shan.

In TABLE 4 data are presented on the age of pebbles of gray porphyroid granites taken from various deposits. As is apparent from the table, the age of all these pebbles is close to that of the mother granite.

TABLE 5 shows the results of age determinations made on sands and sandstones of various geological periods. Almost all these samples were taken in the Issyk-Kul' Lake Basin.

From this table we see at a glance that the majority of the specimens give an age very close to, or completely identical to, the age of Caledonian grani-

toids (370 m. y.). We may conclude that as a rule all the sands and sandstones in this case have the same argon:potassium ratio as the original rocks.

Against this background of a relative uniformity of age, we find some exceptions that require explanation. The composite sample of Tertiary sandstones, as well as individual samples of these rocks, gives a somewhat reduced age. This is apparently due to the fact that these sandstones represent rather porous, strongly eroded material (red-colored deposits) in which secondary clay minerals are present. The same explanation can probably also be applied

TABLE 5

No.	Rock	Site from which sample was taken	K (%)	Ar ( $\frac{\text{cm.}^3}{\text{gm.}} \times 10^{-5}$ )	Age (m.y.)
1	River sand Q	Barskaun	2.78	4.24	365
2	River sand	Tossor	3.40	5.21	365
3	Lake sand (1-2 mm.)	Issyk-Kul' (Barskaun)	3.51	5.29	360
4	Lake sand (1 mm.)	Issyk-Kul' (Barskaun)	2.83	4.72	395
5	Sandstone Q	Issyk-Kul' (Barskaun)	4.43	7.52	400
6	Sandstone Kz	Complete sample, Terskey	2.98	5.03	400
7	Sandstone Kz	Complete sample, Central Tien Shan	2.89	4.21	350
8	Sandstone Tr	Complete sample, Dzhergalan	3.01	3.61	290
9	Sandstone Tr	Dzhergalan (I)	3.18	5.10	380
10	Sandstone Tr	Dzhergalan (II)	2.30	2.58	275
11	Sandstone Tr	Dzhergalan (III)	2.15	2.89	325
12	Sandstone Tr	Dzhety-Oguz	3.09	3.38	270
13	Aleuropelite J	Agulak	1.45	2.20	360
14	Sandstone J	Dzhergalan	1.59	2.36	355
15	Sandstone J	Dzhergalan	2.12	3.17	360
16	Gravelite J	Dzhety-Oguz	0.61	0.95	370
17	Sandstone C	Complete sample, Central Tien Shan	1.89	2.79	355
18	Sandstone	Dzhergalan	3.53	5.30	360
19	Sandstone	Dzhergalan	2.09	2.63	305
20	Sandstone	Dzhergalan	2.59	4.01	370
21	Sandstone	Dzhety-Oguz	1.69	2.40	340
22	Sandstone	Boam Ravine	3.67	4.95	325
23	Sandstone	Boam Ravine	3.28	4.32	320
24	Sandstone	Boam Ravine	1.89	2.79	355
25	Sandstone	Karakiche	1.91	2.48	315
26	Sandstone	Agulak	1.73	2.90	395
27	Sandstone	Kyzyl-Suyek	2.97	5.17	410

to some of the samples of Carboniferous sandstones giving somewhat reduced ages.

The question naturally arises as to how far these observations can be extended to other regions, with other types of weathering and sedimentation. This question is answered to some extent by a comparison of the sandstones of four age groups, C, J, Tr, and Q, formed under different climatic and geological conditions. In all these cases, the age was the same as that of the source material.

It is not possible for us to cite a number of other such examples here. Some will be given in the section dealing with use of radio-active methods of age determination for paleogeographic reconstructions.

*The Argon:Potassium Ratio in Clays*

Examining clays for the purpose of studying their argon:potassium ratios looks at first glance like an unpromising and thankless task, especially since removing radiogenic argon from certain types of clays sometimes is attended by technical difficulties. Nevertheless our experiments have yielded interesting and hopeful results (TABLE 6).

Let us consider the Jurassic clays of the Central Tien Shan, which are typical finely sedimented soils from Carboniferous deposits. Their mineral composition has not as yet been studied in detail, but it has been established that all

TABLE 6

No.	Rock	Site	K(%)	Ar $\left(\frac{\text{cm.}^3}{\text{gm.}} \times 10^{-5}\right)$	Age (m.y.)
I. Central Tien Shan					
1	Gray clay J <sub>1</sub>	Dzhergalan	3.67	4.73	315
2	Gray clay	Dzhergalan	3.05	3.81	305
3	Gray clay	Dzhergalan	3.62	5.50	365
4	Gray clay	Soguty	1.74	2.70	370
5	Gray clay	Soguty	1.66	2.66	380
6	Yellow clay J <sub>1</sub>	Soguty	1.87	2.86	365
7	Yellow clay	Minkush	2.97	4.26	345
8	Recent clay	Barskaun	2.68	3.70	335
II. Karaganda Basin					
9	Gray argillite J	Upper Sokur Trough	2.12	3.44	385
10	Yellow argillite J	Mikhaylov Trough	1.98	2.74	335
11	Yellow argillite	Mikhaylov Trough	1.71	2.50	350
III. Northeast Fergana Pg Clays					
12	Clay	Turkestan Layer	2.40	1.64	170
13	Clay	Alay Layer	3.31	1.66	130
14	Clay	Alay Layer	3.16	1.75	140
15	Clay	Alay Layer	3.36	1.85	140
16	Clay	Alay Layer	3.41	2.01	150

of them contain very fine particles of feldspar and hydromicas. We have examined clays from three different regions hundreds of kilometers apart.

The ages of five clay samples, **3** to **7**, were identical and equal to that of Caledonian granitoids and to the time since the metamorphism of ancient sedimentary rocks. In this case there can be only one answer: the potassium-containing minerals of the Jurassic clays of the Central Tien Shan are (largely, if not entirely) a mechanical sediment. They consist of very fine fragments of crystals of Caledonian granitoids or metamorphic rocks.

Two samples from Dzhergalan, **1** and **2**, gave a more recent age. This age was closer to Hercynian, which might be explained by: (1) admixture of Hercynian material, (2) admixture of potassium-containing secondary minerals, or (3) loss of argon. This case will require further study.

Sample 8 is a recent clay, with a small admixture of sandy material. This clay is a recent redeposited formation, whose age is also close to Caledonian. Samples of Jurassic argillites of the Karaganda Basis gave a similar age. Under the microscope it was seen that these argillites consist mainly of a pelitomorphous mass.

The third group includes the Paleogenic clays of northeast Fergana. In this case the various clay samples give an age close to the Jurassic. It follows that these clays are of markedly different source material from the Jurassic and recent clays of the northern zone of the Tien Shan and Central Kazakhstan. They were apparently formed from more recent rocks of the Pamir region.

TABLE 7  
AGES OF TERRIGENOUS MATERIAL OF VARIOUS SILTS

No.	Station No.	Site	K (%)	Ar ( $\frac{\text{cm.}^3}{\text{gm.}} \times 10^{-5}$ )	Per cent atmos- pheric Ar	Age (m.y.)
I. Iceberg silts in vicinity of Antarctica						
1	185	Off Ingrid Christensen Coast	2.20	4.32	47	460 $\pm$ 45
2	181	Off Ingrid Christensen Coast	2.65	5.64	63	490 $\pm$ 80
3	158	Davis Sea	2.40	4.77	47	460 $\pm$ 45
4	111	Near Davis Sea	3.25	5.40	44	390 $\pm$ 20
5	330	Off Wilkes Land	3.48	10.27	14	650 $\pm$ 30
6	331	Off Wilkes Land	2.84	8.98	26	690 $\pm$ 70
7	51	Off Adelie Coast	2.77	4.02	62	350 $\pm$ 50
8	57	Off Oates Coast	2.12	4.67	61	505 $\pm$ 80
II. Silts of northern and western portions of Indian Ocean						
9	147	Near east Africa	1.10	3.41	18	680 $\pm$ 50
10	327	Bay of Bengal	2.70	2.79	13	255 $\pm$ 15
III. Red silts from the Pacific Ocean						
11	3156	Central zone	1.98	1.20	61	155 $\pm$ 40
12	972	Central zone	2.39	1.41	60	145 $\pm$ 35

Samples made available to us through the kindness of A. P. Lisitsyn.

### *The Argon:Potassium Ratio in Silts*

Since it was explained in the previous section that in the majority of clays the argon:potassium ratio remains close to that in the source materials, it is naturally asked whether this statement also applies to silts.

Ocean silts from deep water have several characteristics that distinguish them from the usual "fragmental" clays. Accordingly, it is of interest to find out how constant the argon:potassium ratio is in the terrigenous portion of silts. TABLE 7 contains some data pertaining to this question.

This table differs from previous tables in having an additional column, "Per cent atmospheric argon." Ages are given with an indication of maximum error since many extraneous gases are removed when silts are analyzed

for argon, and the determination of the argon:potassium ratio is therefore less accurate.

The map in FIGURE 1 indicates several of the ages that we have obtained for silts of the Antarctic region. For a comparison of the age of these silts with the age of the source materials, typical ages of Antarctic rocks are also indicated on the map.<sup>19</sup> The data are still too meager to allow us to determine whether the argon:potassium ratios in silts are completely identical with those in the original rocks; but even in this material we can see in broad outline a definite correspondence between the ages of the silts and that of the probable mother material.

There cannot be complete correspondence between the ages in this case because icebergs carry terrigenous material for considerable distances and a

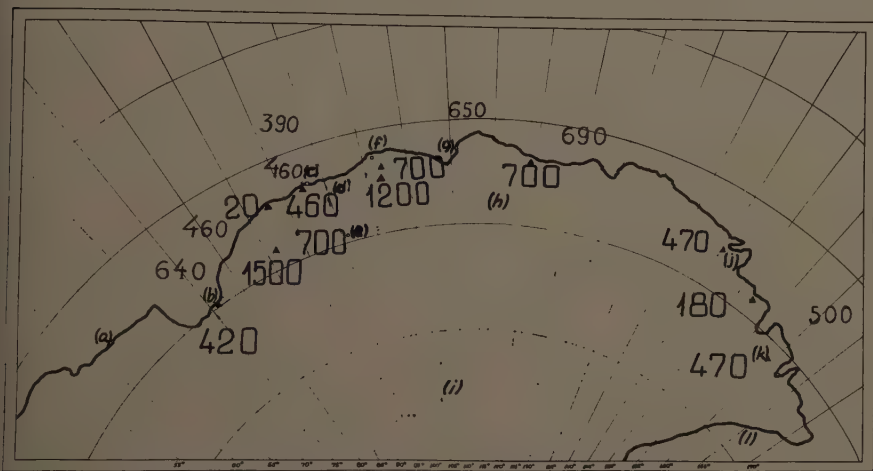


FIGURE 1. East Antarctica: (a) Mawson, (b) Ingrid Christensen Coast, (c) Mirny Station, (d) Queen Mary Coast, (e) Pionerskaya, (f) Oasis, (g) Wilkes, (h) Wilkes Land, (i) Vostok, (j) George V Coast, (k) Oates Coast, and (l) Ross Sea.

certain amount of mixing of this material occurs in silts. In view of this fact, the possibility arises of determining an "average" or prevailing age for Antarctic rocks. The point is that all of Antarctica is covered by a thick layer of ice, and we can infer its geology only from small rock outcrops along the seacoast. In their endless motion toward the ocean, glaciers collect an "average sample" from the continent and deposit it offshore. This "sample" is further mixed by the drifting of icebergs. In a more detailed investigation of the ages of silts, utilization of this fact might be a means of studying the main directions of the drifting of icebergs, both now and in the past (in the latter case, by using the deep portions of the core sample).

From the material obtained thus far, we can estimate the "average age" of the East Antarctic to be approximately 500 to 600 m. y. Pacific Ocean deep-water clays are of more recent age (of the order of 150 m. y.), which is understandable since the Pacific Ocean is surrounded by recent tectonic-magmatic provinces.



For the northern zone of the Indian Ocean, we shall cite only two silt age determinations. Sample 9, taken close to the shores of Africa, is of a comparatively early age; this is natural, when we consider the extensive distribution of Pre-Cambrian rocks on the African continent. The sample from the Bay of Bengal is of later age, probably because of the wearing away of more recent material by the Ganges River.

The few determinations of silt ages cited here indicate that the results are reasonable. It is probable that development of this approach in investigating ages of the terrigenous component of silts may be useful in answering a number of questions in marine geology.

TABLE 8  
VARIOUS FRACTIONS OF FELDSPAR, CLAYS, AND SILTS

No.	Rock	Fraction (size in mm.)	K(%)	Ar ( $\frac{\text{cm.}^3}{\text{gm.}} \times 10^{-6}$ )	Age (m.y.)
1	Feldspar from pegmatites of Northern Karelia	2.0-0.2 (misc.)	11.07	91.5	1450
		0.2-0.1	11.06	95.8	1490
		0.1-0.05	10.90	94.4	1500
		0.05-0.01	11.08	96.4	1510
		0.01-0.001	11.08	93.1	1465
		<0.001	10.80	84.0	1380
2	Jurassic clay of Central Tien Shan	Monolith	2.97	4.26	345
		>0.002	2.70	4.03	360
		<0.002	3.05	4.52	355
3	Clay of Paleogene Maykop Suite (Southern Yergen- geni)	Monolith	2.25	1.61	175
		>0.005	2.00	1.48	180
		0.005-0.001	2.43	1.64	170
		0.001-0.0005	2.40	1.53	160
		<0.0005	2.04	1.42	175
4	Paleogene aleurite clay of NE Fergana (Alay Layer)	Monolith	3.36	1.85	140
		0.1-0.3	3.33	1.86	141
		0.1-0.05	3.41	1.82	137
		<0.05	3.42	1.86	138
5	Red deep-sea clay from Pacific Ocean (Station 3156)	Monolith	2.36	1.52	160
		0.05-0.01	2.28	1.60	175
		<0.01	2.48	1.47	150
		>0.05	1.98	1.20	155

*The Retention of Radiogenic Argon in Clays and Silts and Some Problems  
Concerning Their Composition*

The fact that radiogenic argon is completely (or in any event, largely) retained in the finest subcolloidal particles of clay and silt naturally may generate some perplexing questions. The most serious doubts arise in connection with the following points.

(1) If we regard the potassium-containing portion of clays and silts as a mechanical sediment, then it may appear strange that upon such fine fractionation the inert gas argon is completely retained. Such doubts even appear to be supported by some experiments.<sup>19</sup> However our experiments (TABLE 8) in-

dicating the opposite. As can be seen from this table, in various fractions (down to the subcolloidal fraction) of feldspar, clay, and red deep-water silt, the argon:potassium ratio is almost unchanged.

(2) The study of the mineralogy of clays has now reached an advanced stage of development. A whole series of clay minerals has been established and studied; these minerals are found in almost all types of clays and silts, and it is supposed that in many cases they are the principal constituent. If this is so, then in most instances these clay minerals were formed much later than the original crystalline rocks and, consequently, their age will be much more recent (as late as the Quaternary period). It is uncertain, then, to what extent they are able to retain radiogenic argon. Most important, it is well known that ion-exchange reactions (including ion-exchange reactions involving potassium) readily occur in these minerals.

How, then, is the primary argon:potassium ratio preserved in this case? We cannot consider this question in detail here; moreover, it still has not been studied sufficiently. We will make only the following observations by way of general preliminary remarks. It seems to us that a significant fraction of clays is composed of mechanical sediments consisting largely of elementary crystals ("blocks") of feldspars. In such ideal microcrystals the retention of radiogenic argon should be complete. The role of clay minerals in the composition of clays probably is often exaggerated since their presence is easily diagnosed; the presence of a mechanical "fragmental" component in clays is sometimes disregarded. It is not often that we find thoroughly investigated and characterized clay minerals from known deposits in the form of significant independent accumulations. It is therefore important to point out that most clay minerals contain a very small amount of potassium, and thus can not be, in this instance, an obstacle to the determination of the age of terrigenous fragments. It is true that clay minerals sometimes contain enough potassium. We have obtained the age of formation of certain kaolinites, but this is a special problem beyond the domain of the present article.

As regards adsorption of potassium from water, in preliminary experiments in our laboratory potassium adsorbed from water on clays and silts was not detected in substantial amounts. It is therefore reasonable to suppose that the largest part of the potassium in clays and silts is present in the finest fragments of rocks and minerals. This is indirectly supported by the fact that the age of clays in the Tien Shan agrees with the age of the original material.

(3) Serious objections may arise because of the presence in clays and silts of later deposits of potassium minerals, especially glauconite and products of recent underwater vulcanism.

The presence of these minerals can be readily demonstrated by direct observation under the microscope. In our samples they have not been found in significant quantities. When they are present and it is impossible to remove them, the age of the original material cannot be determined. As yet it is uncertain how high the potassium content in organogenic residues may be. It is probably not substantial, but this problem unquestionably requires special study.

In any case, strongly organogenic silts are a poor object for investigation. They yield many extraneous gases, and the accuracy with which we can de-

termine their radiogenic argon and potassium is greatly reduced. However, silts rich in the mineral component, together with the majority of clays, will apparently yield satisfactory results in determinations of the age of their original material by the argon method, although the accuracy of such determinations will probably be less than it is with pure minerals.

*The Possibility of Using Radioactive Methods of Age Determination for Paleogeographic Reconstructions*

In earlier works we pointed out that, with some accessory minerals of ore slimes, it is possible to determine age by the lead and helium methods.<sup>5,7,1</sup>



FIGURE 2.

The possibility of utilizing pebbles, sandstones, and silts for determining age by the argon method opens up broad vistas for the application of this method for paleogeographic reconstructions. As the first illustration we cite two examples, shown schematically in FIGURE 2.

*The age of sands of the glacial deposits of the Baltic region.* In their invasion of Europe, the glaciers of the most recent glaciation of the Finnish and Scandinavian regions took with them a good deal of rocky and sandy material from the Baltic shield. These fluvioglacial deposits have been studied by many investigators from different points of view. It seems to us that one of the most interesting studies in this area is that of Sederholm, who, on the basis of petrographic indications, established source regions and aureoles of dispersion for

the erratic boulders. Sederholm's scheme is found in many geologic works as a classic model of this type of investigation.

Suppose we follow the changes in the argon age of glacial sands within the limits of Sederholm's aureoles and compare the ages obtained with that of the bedrock in the presumed source region. This will be, on the one hand, an excellent test of the constancy of the argon:potassium ratio under conditions of prolonged transportation of sand by ice, and on the other, an illustration of the applicability of the argon method to such problems.

Let us examine some samples from Sederholm's "South Karelian" and "South

TABLE 9

No.	Rock	Site	K(%)	Ar ( $\frac{\text{cm.}^3}{\text{gm.}} \times 10^{-6}$ )	Age (m.y.)
1*	Rapakivi granite	Vyborg massif	5.88	5.3	1540
2*	Feldspar fraction of Rapakivi	Vyborg massif	7.83	6.5	1450
3*	Granites of the 4th magmatic cycle		—	—	1380
4	Glacial sand	Zelenogorsk	3.40	2.9	1480
5	Glacial sand	Komarovo	2.5	2.2	1520
6	Glacial sand	Sosnovka (Leningrad)	2.63	2.15	1460
7	Coastal sand <0.5 mm.	Mouth of the Neva	2.34	1.82	1390
8	0.5-2 mm.	Mouth of the Neva	2.48	1.95	1400
9	Glacial sand	Moscow	0.40	0.29	1400

\* Data on samples 1 to 3 from E. K. Gerling.

TABLE 10

No.	Site	Rock	K(%)	Ar ( $\frac{\text{cm.}^3}{\text{gm.}} \times 10^{-6}$ )	Age (m.y.)
1	South Sweden	Crystalline rocks			1000
2	Near Lake Kopan'	Dune sand	0.48	2.51	1035
3	Near Lake Kopan'	Coastal sand	0.66	4.07	1170
4	Near Lake Kopan'	Morainic sand	0.78	3.92	1000

Scandinavian" aureoles. TABLE 9 shows our data for the "South Karelian" aureoles.

Samples 4 and 5 were taken from channels in the vicinity of Zelenogorsk and Komarovo, 6 in Leningrad. These are typical fluvioglacial deposits. Samples 7 and 8 were taken from the seacoast at the mouth of the Neva River. These sands have been subjected to repeated redeposition and transfer during the glacial era, and during regressions and transgressions of the Baltic Sea. Nevertheless, the ages of all five samples were very close to the age of the mother granite (1 to 3). Moreover, 9, taken from glacial deposits in the Moscow area (which were carried 800 km. by the glacier), retains the age of the Karelian mother granites.

TABLE 10 shows some data on the age of granitoids and metamorphic rocks

of South Sweden (according to this laboratory, Pre-Cambrian) and coastal and glacial sands from Poland (samples of P. A. Kaplin).

It is evident from TABLE 10 that in this case, too, the age of glacial sands roughly corresponds to the age of the original material.

*The ages of Black Sea sands in various coastal zones.* Let us consider the ages of four samples of Black Sea sand. With this example it is interesting to check, if only schematically, how far the age that is characteristic for the rocks of the mother provinces is preserved in the sands.

From TABLE 11 (FIGURE 2) we see that in its broad outlines, this idea is confirmed.

The age of sample 1 is Hercynian, which is characteristic for most granitoids in the Carpathians. Sample 2 is of a Proterozoic age, determined by the Pre-Cambrian rocks of the Ukrainian shield with an admixture of more recent material. The age of sands in 3 is determined by North Caucasian material but is somewhat older because it is partially derived from the Russian platform.

TABLE 11

No.	Site	Principal source of material	K(%)	Ar ( $\frac{\text{cm.}^3}{\text{gm.}} \times 10^{-6}$ )	Age (m.y.)
1	Near Lake Shagana	Danube River Basin	0.37	0.46	300
2	Near Odessa	Ukrainian shield and (partially) the Carpathian region	0.21	1.07	1020
3	Near Anapa	Northern Caucasus and (partially) the Russian platform	0.79	1.70	500
4	Sulsa district	Transcaucasia	2.23	0.5	50

The sands of 4 gave a tertiary age, determined by recent trans-Caucasian magmatic rocks.

It should be noted that the selection of material for this table was not entirely appropriate, but in this form the rough regularities are quite clearly seen. Thus, after considering all the examples cited above we can affirm that the argon:potassium ratio in sands and sandstones remains very close to that in the original igneous or metamorphic rocks. Consequently, this fact can be used both for paleogeographic reconstructions and for study of the recent migration of sand. Moreover, analysis of age data for older sands can also be useful for understanding broad geochemical problems.

Thus, the data presented above on the age of the source material of sandstones of the Central Tien Shan indicate that, during the entire course of the geologic history of this region beginning with the Ordovician, essentially the same local Caledonian material was worked over. The geochemistry of potassium and argon is a different story, since the migration of these elements has been established in the finest pelitic particles.

Interesting data are obtained from an analysis of the ancient sandstones of the Russian Platform. According to preliminary data, most of these are of Proterozoic age, a remarkable stratigraphic inversion being noted. The geo-



logically older sedimentary rocks are of more recent age than the original materials. This is natural, since erosion and redeposition occurred in precisely that order.

Many such examples could be cited. This is only a first schematic illustration of the productivity of the new direction we are suggesting for utilizing the possibilities of the argon method in determining the ages of rocks and minerals.

### *Conclusions*

Partial conclusions on individual problems have been presented in the appropriate sections. Here we shall only re-emphasize the most important ideas.

(1) In metamorphic rocks, the argon:potassium ratio corresponding to the time of metamorphism is well preserved. This ratio is constant in both the horizontal and vertical directions and agrees with the ratio in intrusions accompanying metamorphism. This makes it possible to utilize the argon method of age determination in piecing together tectonic-magmatic cycles and in making paleotectonic reconstructions.

(2) In the weathering of granitoids, the argon:potassium ratio is found to change in two steps. At first the argon loss exceeds the potassium loss. In the final products of weathering, this difference disappears and the argon:potassium ratio characteristic for the original rocks is restored. The maximum argon loss accompanying weathering ordinarily does not exceed 30 per cent, and more often it is much less. We explain this phenomenon on the basis of the block theory of the structure of feldspars. When the crystal breaks down into blocks, argon is lost from the surfaces of the edges of these blocks. The potassium is held to the edges longer by more stable bonds. It is subsequently "removed" during the rougher treatment of the crystal in the process of migration.

(4) In the process of division of feldspar, no substantial loss of argon is observed. Argon is held in particles of feldspar, clays, and silts with diameters of less than 0.001 mm. This is the size of the subcolloidal fraction. In our case, this is probably the size of the elementary blocks of feldspar.

(5) In granite, pebbles, sands, sandstones, terrigenous clays, and silts, in the majority of instances, an argon:potassium ratio corresponding to the age of the original material is preserved. Consequently, from these it is possible to determine the age of the mother material by the argon method. This opens up a new and additional way of answering a number of questions in lithology, marine geology, and paleogeography.

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### Part III. The Phanerozoic Time Scale

#### THE PHANEROZOIC TIME SCALE: INTRODUCTION

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This part of the monograph begins with a discussion of the Post-Cryptozoic Geological Time Scale. First, however, I shall make some remarks on nomenclature. The term Pre-Cambrian, while thoroughly implanted in the geological literature, is a most unfortunate one. For the subject of this section, for example, it would be necessary to use "Post-Pre-Cambrian." Looking back into the other suggestions that have been made in this monograph, I think M. Kay's suggestion of "Protozoic" for Pre-Cambrian rocks probably has priority but, as he agrees, this can be confused with Proterozoic. I believe it was W. Chadwick who first suggested "Cryptozoic" in place of "Pre-Cambrian" and "Phanerozoic" for Paleozoic and later time. These terms have been adopted by J. Rodgers in his book on stratigraphy and appear superior to the perpetuation of the term Pre-Cambrian. The title for this part of this publication has been defined accordingly.

The discussion of the calibration of the time scale is separated into three eras: Cenozoic, Mesozoic, and Paleozoic. The various workers who report here have largely confined their researches to one of these three intervals of time so that we can consider the accuracy of the individual points proposed and then consider the era as a whole.

For purposes of clarity each speaker notes the decay constants used.

## CRITICAL POINTS IN THE CENOZOIC

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The dates in the present discussion have been computed using the new constant:  $0.585 \times 10^{-10}$  years<sup>-1</sup> for  $\lambda_e$  and  $4.72 \times 10^{-10}$  years<sup>-1</sup> for  $\lambda_\beta$ .

The post-lower or basal-Cambrian (whatever the basal Cambrian is) time scale is of most interest to those who are dealing with rate problems and, for this reason, we wish to obtain as accurate a post-lower-Cambrian time scale as possible. For that matter, we desire a very accurate total time scale. However, for dealing with the various rate problems that are of interest to geologists and paleontologists in particular (such as rates of mountain building, of peneplanation, of evolution, and of dispersal rates of faunas and floras), we shall need a very accurate time scale.

The present time scale, as is generally known, is based on the law of superposition and, within any one continental area, this time scale is very good. I think it probably will not be improved. Alternatively, I think enough study has now been done to have few major changes within any one continental area.

Correlations between continents, however, are somewhat puzzling. The time scale has been developed haphazardly by individuals working in certain areas, finding good exposures of particular beds and defining them as type sections. Others, coming along later to other areas, often with better exposures and better sections, have tried to correlate with the original type sections. Some of the assumptions that have gone into such correlations are questionable today. For example, it was originally believed that the major era, period, and epoch boundaries were those of world-wide orogenies. We are not certain today whether there have been world-wide orogenies bounding all of these so-called era, period, and epoch units; nevertheless, to these probably imaginary boundaries we are now trying to pin accurate dates. It appears that we are getting to the point technically where we should examine the accuracy that we hope to obtain and the accuracy that we possibly can obtain.

If we look at the technical part first, it may be seen that we are rapidly approaching a limit to the accuracy of the decay constants. If we can only know or determine these to an accuracy of 1 per cent and if we expect to date a mineral or rock by 2 different decay schemes, our possible error becomes 2 per cent. I doubt that we shall attain this precision; therefore in the range of the Paleozoic, just from lack of agreement within 2 per cent of the decay constants, we can know only within 5 or 6 million years (m.y.) where any of these major boundaries are, even if these boundaries can be correlated precisely.

We have seen that certain minerals, particularly the glauconites and clays, as reported by P. M. Hurley,<sup>1</sup> are not going to be very good for correlation. The inheritance errors are too large. They are certainly much larger than we can expect from the errors in our decay constants. Therefore we must reduce them, and about the only way to reduce them is to use minerals contained in volcanic rocks interbedded with strata containing fossils. The volcanic rocks must be fresh of course.



Throughout the different geologic sections—particularly type sections—of the world, there are few volcanic rocks near paleontologic boundaries. We must therefore interpolate or extrapolate from the few volcanic rocks that can be dated to these boundaries. The accuracy of that interpolation will depend upon various factors and is not apt to be high in most cases, but interpolation has been done—and I think in the only way that it can be done properly—by Folinsbee, Lipson and Baadsgaard (elsewhere in this monograph) on the tuffs near the boundary of the Cretaceous and Tertiary. They add  $\pm 3$  m.y. to their figure of 62 m.y. for this boundary, which gives an idea of what they think the accuracy of their interpolation is.

That figure is for North America. We must consider now correlation with the type section in Europe, and this problem brings in paleontology. How accurately does the Upper Cretaceous fauna or flora used correlate (in time) with the type section?

Until now this has been a subjective question. Some paleontologists think that dispersal rates, particularly of vertebrate faunas, are extremely rapid and that perhaps in certain cases it has not taken 1 m.y. for a particular species to follow a migration route to another continent and intermigrate back and forth.

This is a question, however, that I think the paleontologists cannot answer accurately until we give them some figures. Therefore there is going to be a juggling of interpolated dates back and forth as paleontologists adjust their ideas to fit physical dates and as we adjust our ideas to the correlations that the paleontologists make.

It does look from preliminary work as if the error in paleontological estimates, in some cases at least, is going to be of the order of 5 or 6 m.y. If this proves to be the case, it is within the limit of accuracy of physical measurement of dates in the Paleozoic. Therefore correlation, for example, of Devonian in Australia with Devonian in England will be, on the basis of the dates that we might get, within this limit of accuracy, and the paleontologic error would go undetected. This condition provided, we can obtain very accurate dates from, for example, Devonian in Australia and Devonian in the type locality of both its base and top.

This is probably as much as we can hope for in the Paleozoic. When we get to the Tertiary, we can certainly measure more accurately than 5 or 6 m.y. Here, I think, we can very precisely define or correlate with type sections, the precision being of the order of perhaps 1 or 2 m.y., even with all the other possible errors of interpolation between datable points within type sections or between correlated points outside of type sections and type section faunas.

The best type of paleontologic material for making such correlations probably will be land vertebrates. However, the great mass of strata of the world is marine and contains invertebrates. We must then make a correlation between the vertebrates predominantly in continental deposits and the marine invertebrate deposits. Here again, there is a chance for error, although I think this can probably be reduced satisfactorily.

There is a problem in the two environments that is different for each. Marine environments are usually of much broader extent than continental environments. The continental is dominantly one of rapid subsidence adjacent to



rapidly eroding highlands. In order to get a datable point, the point has to be preserved. The continental basins are for the most part fault block basins in which the sides are steeply bounded.

In this situation there is a series of continental beds that thicken toward the fault and thin out away from it. Most of these blocks tend to be hingelike in action, although there are some true grabens, such as the Rhine graben, that have dropped down between both sides. This is very characteristic of most continental-type environments.

If we use for dating purposes volcanic material that has accumulated in such an environment, we have for the most part two major possibilities: either suitable flows, that is, those containing either biotite and/or sanidine or orthoclase, or tuffs containing these minerals. Tuffs are explosive products of volcanic eruptions and are more widespread than flows, the latter usually being closely connected with their sources. Tuffs, being more widespread, are probably the better material, generally speaking.

The problem then is one of contamination, because a tuff deposited in a basin often will also be deposited on the local highland mass immediately adjacent to such a basin. Within hours of the time that such a tuff is laid down from the air, it is being stripped by erosion, and volcanic detritus is being immediately transported down the slope and into the basin. Therefore collection of such material must be done carefully to avoid contamination from weathered older basement rocks that may be exposed on either the adjacent volcanoes or the slopes of fault blocks.

This collection requires certain criteria for recognizing contamination, about which I am uncertain. We have now dated a number of tuffs (in fact, almost all of these dates presented are from tuffaceous material), and we have had a large number of dates invalidated because of contamination. How do I know they are contaminated? If a date of 100 m.y. is obtained repeatedly from samples that are Pliocene and fragmental particles that look as though they might be foreign are recognized, it is reasonably certain that they are contaminated. This contamination probably occurs by erosion as soon as the eruption is over. The volcanic material adjacent to the basin is stripped and immediately to this is added the underlying basement material; therefore the upper parts of most tuffaceous beds are suspect. Collection must be made only from the lower parts, the lower third of such beds. These beds may appear to be pure and superficially the same throughout, but I have seen several such beds that looked identical from top to bottom yet gave different ages from top to bottom, the younger age being on the bottom.

This is not usually the case with pyroclastic breccias or with lava flows but, as I have said, these are also very limited in extent and often not found with fossil beds. Tuffs usually are. I think that tuffs, being almost world-wide in extent sometimes, are perhaps our very best datable strata.

The matter of correlation is my next concern. I think it is necessary to obtain, within one geologic province, datable points as close together as possible and through as much of the stratigraphic section as possible. Only in this way can we define the limits of faunal stages. We have chosen one such province that is particularly favorable, the Western Great Basin in the United States,

which has a great number of volcanic beds interbedded with fossil-bearing strata. From here we shall expand to the next province or work them concurrently if we can get people to take part of the problem. As a start, we have begun work on the Miocene and Pliocene of the Western Great Basin. We hope to go from here and adjacent areas to Europe. We have collected in parts of Europe, but much of the material is contaminated. Therefore our correlations here are strictly those of the local faunas of western North America as defined by the Woods Committee in 1941.<sup>2</sup> The correlation with the European vertebrate faunas is not precisely known, but is shown as it is believed to be by the Woods Committee. Our next step will be to try to get points in the vertebrate scale of Europe in order to relate those data, and from there go to the marine section containing invertebrates. Even in western North America, the relationship between vertebrates and invertebrates is very inadequately known. Certainly, the error can be of the order of 3 or 4 m.y.

TABLE 1

Type locality	Age (m.y.)
Lower Hemphillian, Nev.	9.1
Clarendonian, Calif.	10.6
Clarendonian, Nev.	11.1
Clarendonian, Nev.	11.2
Clarendonian, Nev.	12.0
Barstovian, Calif.	15.2
Barstovian, Calif.	15.2
Hemingfordian, Calif.	17.3
Arikareean, Neb.	21.6
Whitneyan, Ore.	25.7
Chadronian, Texas	33.1

In TABLE 1 are our dates of the Miocene and Pliocene with one or two lower in the sequence. Starting at the top, the Hemphillian from far western Nevada is, according to vertebrate paleontologists, the longest in time of the Tertiary ages, and the date of 9.1 m.y. is probably at the very bottom of the Hemphillian that probably extends upward to  $\pm 2$  m.y. at the base of the Blancan.

We have a date of 2 m.y. from the Blancan that has a very high error (ca.  $\pm 10$  per cent or perhaps even higher). I have not included it because we are re-determining it.

The Clarendonian date of 10.6 m.y. is probably very near the top of the Clarendonian. The Clarendonian date of 12.0 m.y. (both of these are from Nevada) is right at the very bottom of what vertebrate paleontologists define as Clarendonian; and, if this be true, 12.0 m.y. should be the very base of the vertebrate Pliocene or top of the vertebrate Miocene. This fauna as described by one of us (D.E.S.) is called Barstovo-Clarendonian. This is probably a very important point from the vertebrate-faunal view.

The Barstovian date at the type locality, a little north of Barstow, Calif., will also be an important point. We have measured it twice and obtained the same date both times. The 15.2 m.y. date about 70 miles away in the mountains

southwest of Bakersfield was obtained from a tuff containing an almost identical fauna.

It is just possible, therefore, that we have not only identical faunas but have dated the identical stratum. Since these rocks are highly deformed at this place and discontinuous, we cannot correlate them by mapping.

Dropping now to the Whitneyan and Chadronian, the Chadronian from Texas is not the type locality of the Chadron formation. It was named Chadron Tuff by Stovall<sup>3</sup> who correlated it with Chadron in Nebraska. This correlation, although based on a large fauna, may or may not be the best basal Oligocene. We expected the base of the Oligocene to be somewhat older than this. It is interesting, however, that, taking R. E. Folinsbee and J. Lipson's Paleocene-Cretaceous boundary of 63 m.y., this Chadronian date is almost halfway between, that is, it just divides the Tertiary. Also, it is surprising and perhaps of no significance that the Tertiary stages below the Chadronian equal in number the Tertiary stages above the Chadronian; however this dividing point may be very close.

The Whitneyan from the John Day Basin in Oregon is from very nearly the bottom of the sequence, actually 60 or 80 ft. above the bottom of the sequence. Unfortunately, this is not a primary volcanic mineral. It is authigenic sanidine replacing part of the tuff, and we are assuming that the replacement took place very shortly after deposition and we therefore think this is probably a good date.

We are getting other material currently from this site that, of course, can only be somewhat older; how much older we have no idea.

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### Discussion of the Paper

J. L. KULP (*Lamont Geological Observatory, Columbia University, Palisades, N.Y.*): Before discussing these dates and the general problem of the Tertiary scale, I think we should mention such other dates as are relevant. There are only a few.

The Vakis-Jvary locality in Georgia, Union of Soviet Socialist Republics, has been determined by M. M. Rubinstein. It is a granite that cuts fossiliferous middle Eocene and is overlain by fossiliferous lower Oligocene. Geologists feel that the granite intrusion occurred shortly after the middle Eocene.

The Central City, Colo., pitchblende has been run by many people and there are quite a range of ages but, on the freshest material, there is a clustering of ages around  $58 \pm 2$  m.y. and very few higher than that. There are a few that are quite a bit lower, one which is as low as 35 m.y., probably a result of lead-loss. T. S. Lovering has reviewed the geological setting and feels that it is most likely near the Paleocene-Eocene boundary. Accepting R. E. Folinsbee's

date of 63 to 64 m.y. for the Cretaceous-Paleocene boundary would indicate that the Paleocene was only about 5 m.y. long. We have dated one phase of the Boulder Batholith, Colo., and obtained  $71 \pm 2$  m.y.

R. E. FOLINSBEE (*University of Alberta, Edmonton, Alberta, Canada*): We have dated biotite from the Boulder Batholith too and have obtained 78 m.y. The Boulder Batholith, according to Knopf, who is more of an expert perhaps than anyone, is a composite intrusion with 5 phases. The phase we dated is the Clancy granodiorite, one of the earlier phases, and 78 m.y. puts it well back into the Upper Cretaceous.

J. Lipson really should be giving these comments; but we have one Tertiary date in the Mid-Miocene, the Snoqualmie Batholith. This batholith was dated stratigraphically with fair accuracy first by Smith and Calkins in 1906; their work has been confirmed by Grant in 1941. The Snoqualmie granite intrudes late Oligocene volcanics that contain the John Day vertebrate fauna and hence can be assigned to the Miocene.

We have 3 runs on the Snoqualmie biotite: 16.3, 17.0, and 17.7 m.y., average 17.0 m.y., and this fits exactly with the work done on other late Tertiary (Alpine) intrusives.

I think these are really all the dates that are pertinent to the Tertiary. The rest I shall discuss in connection with the Upper Cretaceous data.

KULP: Does anyone else have a contribution in terms of dates?

CURTIS: We have also dated the Clancy and Boulder Batholiths and we have obtained several dates; 78 m.y., I think, is our best.

J. LIPSON (*University of Alberta, Edmonton, Alberta, Canada*): I wanted to ask Curtis about looking at these tuffs and being able to guess whether they have older material in them. I am surprised. You mean you cannot look at the thin sections of the material under the microscope and make any guess until you suddenly find that it is 100 m.y. old?

CURTIS: This becomes complicated. It depends upon the type of eruption. There are eruptions that blow out a great deal of foreign material from along the sides of the vent. In the Berkeley Hills, for example, behind the University of California campus, there is a tuff that is very thin and looks the same from top to bottom. It contains fragments of all the older rocks found beneath it.

To look at it, you would say that it is detrital material that has been collected. Actually, it turns out that the vent itself is exposed, and in the vent or conduit—where the rocks are tilted at 60 degrees and therefore the conduit can be seen for some vertical distance—may be seen the same material filling the conduit, brecciated fragments of Tertiary, Cretaceous, and possibly much older ages. There is some material here that we do not see in surface exposures for 100 miles around.

We have not dated this yet but soon shall, so I do not know whether this is going to be usable. It is possible that the eruption was so rapid that the material was not heated, and the radiogenic argon was not driven out of the older rocks that contain a high quantity of both biotite and orthoclase, in which case the age will be no good. If, however, these fragments were intensely heated for a short time before and during the eruption, all older radiogenic argon will have been removed and the date will probably be all right.



In other cases where such a vent is not seen, it cannot be certain whether foreign material has been admixed after or, as in the case of welded tuffs, heated sufficiently so that all radiogenic argon has been eliminated.

Some of the samples we got from Europe were filled with fine fragments of granitic rocks, including much of the Miocene and Pliocene from Germany, but we were told that they were all tuffaceous.

However, in thin section these were holocrystalline fragments and were clearly not part of the primary volcanic minerals, that is of primary magma, therefore when the age obtained, which was supposed to be in the range of 15 or more m.y., came out 70 m.y., it was no surprise to us and, since the whole sequence of samples ranging from Lower Miocene up to Pliocene contained the same granitic fragments, we did not date any more.

In other cases, you can see actual rounding of grains and, of course, these become suspect at once since, if material has been rounded, it has probably been transported along the surface.

Each case must be dealt with individually, and every possibility must be considered. I think perhaps the easiest part of this is getting the date. The final evaluation has to come later. Therefore it is necessary to obtain as many data bearing on the origin of a sample as possible.

G. J. WASSERBURG (*California Institute of Technology, Pasadena, Calif.*): We are in this case considering two opposing effects, one a loss-of-daughter product and the other inheritance. Just how do you know when you have the right answer? You must have some a priori criteria.

FOLINSBEE: There is an answer, I think, in that we have been dating sanidine-biotite pairs. Sanidine is very easily identified optically. It is unlikely that sanidine would survive through an erosional cycle. If a pure sanidine fraction is obtained from the sample, then there is much more certainty that the biotite is volcanic. The biotite otherwise could be interpreted as rafted in by erosion from older intrusives. These are the criteria we have applied. I am sure that Curtis is applying somewhat the same criterion.

CURTIS: A knowledge of the possible source of contamination is desirable but, in answer to your first question of the necessity for some a priori consideration, this will not bother geologists as much as it will physicists. There is a certain resonance here. We get some new data, go back to the first conclusions and correct them, and then go back to the other data and conclusions and correct them. This is the way a great deal of geology has developed and must develop. There are certainly criteria that can be established but, if you go strictly according to rules, you get into trouble right away. I do not think that this is always possible or wise.

One of our samples involved just what Folinsbee said, that is, that we should be able to distinguish sanidine. It so happened that the basement rocks near the sample contained sanidine, and these basement rocks were very much older than the material that we were trying to date. There was no way of distinguishing the two sanidines. Optically they both were the same. Therefore, we had to throw that sample out when we got an anomalously old date.

As dates get younger and younger, this problem becomes more and more difficult to solve. The African material from Olduvai Gorge that we are work-



ing on now, perhaps most interesting to anthropologists, is a sequence of tuffs. We have had numerous reversals in the sequence owing to what appears to be very small amounts of contamination.

In some cases we have been able to separate the contamination and get two distinct ages, but I think we shall have to go back and collect the whole sequence more carefully. This is why I have not used some of these data. We can put a fairly close boundary between Pleistocene and Pliocene on the basis of the Olduvai material, but I think we should wait until we get more samples before publishing this date.

However, much of that section is contaminated. I have tried every possible way to distinguish what can be contaminants. I think I have spotted some things, but I think the thing to do is to get a sequence of dates and throw out those that are vastly anomalous.

P. M. HURLEY (*Massachusetts Institute of Technology, Cambridge, Mass.*): I agree with Wasserburg that this is an important question. These tests are made on known material, but before long investigators will turn around and use this knowledge in attempts to measure unknowns. Years ago we were puzzled by some values given by minerals in tuffaceous rocks when we were measuring helium age ratios in zircons that had suffered very low total  $\alpha$ -radiation damage. I can say now that the Zr-He method under these circumstances is an excellent one, particularly for young zircons. However, we started to measure the age of some late Tertiary zircons separated by E. S. Larsen from acid tuffs in the San Juan, Puerto Rico, volcanic complex. There was no chance of material being rafted in to this area, which is a large one with sections of volcanics all more or less of the same age. As I remember it, the zircon samples from Pliocene tuffs showed an age of about 80 m.y. We were never able to find a reason for this and dropped the question. Nevertheless, it raised doubts on the use of phenocrysts in explosively effusive material. As a result I suggest that it would be important to report all anomalous results.

KULP: I think, however, with regard to the phenocrysts that surely this would not affect the K-Ar ages.

HURLEY: That is correct in this case.

H. FAUL (*United States Geological Survey, Washington, D.C.*): I have another date to mention here. It is a Middle or Late Eocene carbonatite from the Bearpaw Mountains in Montana. The rock contains large ( $> 10$  cm.) books of biotite that give a K-Ar age of 52 m.y.

P. E. DAMON (*University of Arizona, Tucson, Ariz.*): May I make a comment on contamination. Sabels, a graduate student at the University of Arizona, has been studying the thermoluminescent properties of a tuff that underlies the San Francisco Volcanic Field. It has its origin in the Verdi Valley, Calif., and Sabels thinks he can correlate it into the Bidahochee Formation in the Hopi Butte's country within the Navajo Reservation in Arizona.

I do not believe that the thermoluminescent method is a precise method of dating. There are many problems involved in the crystal chemistry. However, Sabels found in the uncontaminated tuff that he had a characteristic pattern, that is, both shape and the height of the thermoluminescent peak. However in the contaminated tuff the pattern was radically changed.

Therefore, I suggest that, although the thermoluminescent method thus far has given no indication of being a precise method of dating, it might be used as an indicator of contamination.

Incidentally, this work of Sabel was performed at the University of California at Los Angeles, Calif., under the guidance of George Kennedy.

S. C. ROBINSON (*Geological Survey of Canada, Ottawa, Ontario, Canada*): May I ask if any work in these more recent stages, I should say in the Tertiary, has been tied in with paleomagnetism. I wonder if that sequence might help out.

KULP: Not that I know of. Does anyone wish to comment on that?

WASSERBURG: I have two questions. First, how precise is the stratigraphic correlation from basin to basin in California and Nevada? Second, just what sort of interval consistency do you obtain when you date different samples of the "humpty-dumpty" formation taken from a geographic region of many miles? This error may well determine the ultimate significance of the figures.

CURTIS: Most of these dates are from material that has been described in the literature, principally by Axelrod (1956), who has a paper on the "Mio-Pliocene Flora of Nevada and California." These basins are extremely small. I collected this material in all cases except the Whitneyan (collected with D. E. S.). Savage took me to the very places where he obtained his vertebrate faunas. I can say that most of these formations can be mapped only from one to five miles. Then you go across a mountain range and you are in another basin. The same tuffs may extend across, but you cannot be sure that they are the same. They all look very much alike, but the local formations containing the tuffs are entirely different 10 miles apart across a mountain range. You are mapping different units, and the whole structure looks different.

Contrast this with units in Australia in which one bed three feet in thickness was mapped for 400 miles. It is an entirely different problem.

The vertebrates that are involved here in the Great Basin are in some cases almost identical faunas from one basin to another. Savage has chosen to call them local faunas rather than to correlate them as being of one time zone. These individually (the dates that I have given) are called local faunal dates rather than age dates.

For instance, I have given four dates for the Clarendonian. The total will probably be called the Clarendonian stage.

S. S. GOLDICH (*United States Geological Survey, Washington, D.C.*): With regard to the Californian tuffs (tōōfs) and our tuffs (tûfs) in the middle west, there has been a great deal of work in the Geological Survey on the problems of welded tuffs, or tuff flows, and I am very happy to say that this work goes beyond problems of classification and nomenclature. Much of this work will be published in the near future. A review article on the welded tuffs is now available.

The point is that we hope this work will permit us to estimate the temperature of emplacement of some of the welded tuffs, and this information will be quite valuable in studies of dating. There is no question that there is a very large amount of extraneous material in an ejection which we commonly call a *nuée ardente* or Peléean type.

If geologists are able to tell us something about the temperature of the welding of the tuff, we might be in a position to know whether we can expect inherited argon from older sources.

I have one question about the Chadron of Texas. What did you date?

CURTIS: This was sanidine from what has been named by Stovall the Chadron Tuff along the border of the Rio Grande River. At this locality, I think within a few feet of the tuff, is an extensive lower Oligocene fauna.

The problem of welded tuffs is something else again, and I think that the answer is that they have all been heated sufficiently to drive off inherited argon, if you call it that.

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# POTASSIUM-ARGON DATES OF UPPER CRETACEOUS ASH FALLS, ALBERTA, CANADA\*

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## *Introduction*

It appears that volcanic rocks and, indirectly, intercalated sediments, may be accurately dated by the K-Ar method using techniques developed in the dating of micas from plutonic igneous rocks. This paper presents results obtained in a study of ash falls in the western Canada sedimentary basin.

## *General Geology of Cretaceous Sedimentary Basins of Western Canada*

During the later part of the Lower Cretaceous (Albian) an Arctic sea advanced down what is now the MacKenzie valley and gradually spread out over the plains region of western Canada (Stelck, 1958). This is part of a world-wide transgression of the Cretaceous epeiric seas that, as Rastall (1941) mentions, although often called the Cenomanian transgression, began before the Cenomanian epoch. By the start of the Cenomanian epoch (fish scale horizon) this sea covered much of western Canada (FIGURE 1).

About the middle of the Cretaceous period the Cordillera to the west of the Alberta basin underwent profound orogeny (Baadsgaard *et al.*, 1959); this was to continue through the Upper Cretaceous epoch and on into the Tertiary. Explosive volcanic ash from vents such as the Three Sisters plug in the Big Belt Range, Montana (Lyons, 1944) spewed trachytic and rhyolitic volcanic ash eastward into the epeiric seas. These ash beds (bentonites) became intercalated with marine shales of a Cretaceous sea that eventually spread from the Arctic to the Gulf of Mexico, containing a rich and varied marine fauna including European ammonites that can be precisely stage dated. Since many of these ammonites were swimmers, travel time of certain species can be taken as negligible, and Arctic ammonites provide intercontinental index fossils. In late Albian time the boreal link was broken and faunas became more isolated. However, the dated Crowsnest volcanic zone on Mill Creek lies just 200 feet below the world-wide basal Turonian marker bed—the *Inoceramus labiatus* zone (Glaister, 1958)—indicating an open sea connection. Warren and Stelck (1959) have recently described the evolutionary trends in some of these isolated ammonite faunas.

By late Cretaceous time (FIGURE 2) the Cretaceous seas were retreating southeastward as rising highlands began to spill more and more delta-building debris into the basin. The Arctic connections were cut off, but ammonites were still able to get into the northern epeiric seas via the Gulf of Mexico and Atlantic coastal plain. Landes (Russell and Landes, 1940, pages 186 and 187) reports the type upper Campanian ammonite *Acanthoscaphites nodosus* in the Bearpaw shale, although above the Bearpaw bentonite No. 1 that we have dated.

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The Kneehills tuff zone of the upper Edmonton or Battle formation (Russell, 1950) is a very widespread zone of volcanic ash associated with a characteristic white and dark bentonitic clay bed (Sanderson, 1933; Ritchie, 1958; Elliott, 1958). The Kneehills zone marks the transition to Lance beds and introduction of *Triceratops*, *Tyrannosaurus*, *Ankylosaurus*, and *Thescelosaurus*, a marked break in the saurian fauna; it is an excellent widespread marker bed.



FIGURE 1.



FIGURE 2.



Uppermost Cretaceous time was one of abundant coal formation with bentonite interbeds (Pembina or Ardley seam); these bentonites are the latest datable Mesozoic beds in Alberta. By Paleocene time the sea had retreated to the Missouri River area (Cannonball formation), and continental Tertiary sandstones were being deposited over the partially eroded upper Edmonton surface (Elliott, 1958).

### *Sample Preparation and Methodology*

Bentonites are composed mainly of the clay mineral montmorillonite. Sanidine and biotite cleavage fragments ejected from the volcano and carried along with the dust may be released from the bentonitic clay by suspending the bentonite in a blender and decanting the clay fraction. The grit fraction is wet-screened and various size fractions treated by a combination of magnetic and gravity methods. Using a Frantz isodynamic separator and tetrabromoethane-acetone mixtures in a centrifuge and separatory funnels, it has been possible to separate essentially pure sanidines and biotites from the bentonites under study. Potassium in one aliquot of the mineral separate is determined gravimetrically using J. Lawrence Smith fusion followed by tetraphenyl-boron precipitation of the potassium; this result is normally checked by flame photometer. Argon in another aliquot is extracted and purified by a conventional flux-fusion technique. Isotope dilution with mass spectrometric isotope-ratio analysis is used to determine the amount of  $\text{Ar}^{40}$  in the purified gas (Baadsgaard *et al.*, 1957). The  $\text{K}^{40}$  content of the samples is calculated from the total potassium using the abundance ratio  $\text{K}^{40}/\text{K}$  normal = 0.0118, atomic per cent (A.E.C. Nuclear Data Tables, 1959). The constants employed in calculating the ages were:  $\lambda_e = 0.589 \times 10^{-10}/\text{yr.}$ ,  $\lambda_\beta = 4.76 \times 10^{-10}/\text{yr.}^*$

### *Results*

Results are tabulated in TABLE 1; best values are presented graphically in FIGURES 1, 2, and 3. There is considerable scatter in the data, believed to reflect analytical error in potassium and argon measurements. We consider the possible errors in  $\text{Ar}^{40}/\text{K}^{40}$  ratios to be of the order of  $\pm 5$  per cent; their magnitude may be minimized by making duplicate runs.

There is no evidence that sanidines lose radiogenic argon by diffusion; the cogenetic biotite-sanidine pairs give dates substantially in agreement. For convenience in discussing and presenting the data we have used an average "best value" taken to the closest million year; the precision, however, is not believed to be that good.

The measured intervals presented have been obtained from a variety of sources. From a biotite-rich bentonite bed in the middle Albian Harmon shale at Hudson Hope, B.C., C. R. Stelck (personal communication) reports a thickness of 2925 feet of sediments to the first appearance of the Upper Cenomanian ammonite *Dunveganoceras*. This same ammonite genus appears 15 ft. above the Crowsnest volcanic zone on Mill Creek, southern Alberta (Stelck, personal communication).

\* These constants yield essentially the same isotopic ages as  $\lambda_e = 0.584 \times 10^{-10} \text{ yr.}^{-1}$ ,  $\lambda_\beta = 4.76 \times 10^{-10} \text{ yr.}^{-1}$  and  $\text{K}^{40}/\text{K} = 0.0119$  atomic per cent.

In a well drilled at Lethbridge, Alberta, Imperial Oil, Toronto, Ont., Canada reports a drilled interval of 3180 ft. between Bearpaw bentonite No. 1, 45 ft. above Bearpaw-Belly River contact (Russell and Landes, 1940) and the Red Specks, presumed Crowsnest volcanic equivalent (Thompson and Axford, 1953).

TABLE 1  
POTASSIUM-ARGON DATES OF BIOTITES AND SANIDINES FROM CRETACEOUS BENTONITES,  
WESTERN CANADA SEDIMENTARY BASIN

No.	Horizon and locality	European stage	K <sup>40</sup> ppm.	A <sup>40</sup> /K <sup>40</sup>	Date* m.y.
	<i>Pembina coal seam, Whitecourt, Alberta,</i> 54°05'N, 115°31'W	Maestrichtian (upper)			
AK-127	Biotite		3.84	0.00376	63
AK-128	Sanidine		10.74	0.00386	64
	<i>Kneehills tuff zone, Strawberry Creek,</i> <i>Alberta, 53°16'N, 114°07'W</i>	Maestrichtian			
AK-19			7.79	0.00396	66
KA-154	Sanidine (varying purity separation)		8.50	0.00396	66
AK-102			9.63	0.00408	68
KA-155			1.32	0.00393	66
AK-20	Mica (biotite, altering to vermiculite)		0.46	0.00391	65
	<i>Bentonite No. 1, Bearpaw shale, Leth-</i> <i>bridge, Alberta, 49°42'N, 112°53'W</i>	Upper Campa- nian			
AK-11	Biotite		6.03	0.00408	68
				0.00464	77
AK-92			7.05	0.00444	74
AK-22	Sanidine (varying purity separation)		5.48	0.00457	76
AK-93			10.56	0.00462	77
	<i>Crowsnest volcanics, Coleman, Alberta,</i> <i>Agglomerate. 49°39'N, 114°31'W</i>	Cenomanian			
AK-2	Sanidine (½" phenocrysts) Alberta,		12.76	0.00567	94
KA-22	Berkeley		13.06	0.00540	90
	<i>Mill Creek, Alberta. Bentonite. 49°25'N,</i> <i>114°09'W</i>	Cenomanian			
AK-97	Biotite		6.88	0.00596	99
AK-98	Sanidine		10.69	0.00609	101
	<i>Harmon Shale, Hudson Hope, B.C.</i> 56°07'N, 121°48'W	Middle Albian			
AK-0	Biotite (chloritized from tuff)		3.00	0.00726	119
				0.00695	115

Constants:  $\lambda_a = 0.589 \times 10^{-10} \text{ yr.}^{-1}$

$\lambda_\beta = 4.76 \times 10^{-10} \text{ yr.}^{-1}$

$K^{40}/K = 0.000118_1$  atomic per cent abundance.

\* Assumed deviation in dates is  $\pm 5$  per cent.

Ower (1958) reports the interval from Bearpaw bentonite No. 1 to Kneehills as 1225 to 1340 ft. This is remarkably consistent throughout the whole of central Alberta and western Saskatchewan (Loranger and Gleddie, 1953). From the Kneehills tuff zone a maximum of 400 ft. of beds occur in the Edmonton area before Tertiary (Paskapoo) sandstone deposition. The Pembina or Ardley seam at Whitecourt lies 200 to 300 ft. above the Kneehills tuff zone. Ower (1958) does not believe there is a marked erosional hiatus in this area. Russell (1950) has made a critical correlation of the Cretaceous-Tertiary

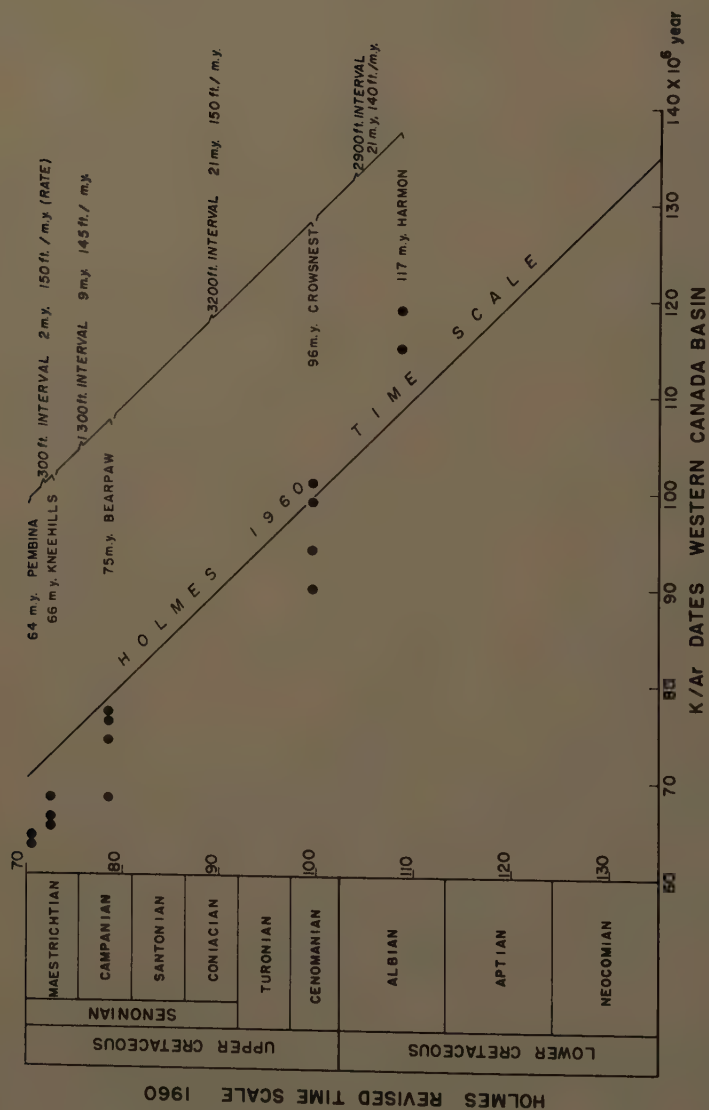


FIGURE 3.

transition in general agreement with Ower's study of the Edmonton formation, and a painstaking study has recently been made by Elliott (1958).

There is a remarkable uniformity in the apparent rate of deposition of sediments in the Alberta and Peace River basins from Middle Albian to upper Maestrichtian time, if the measured thicknesses are divided by K-Ar date-time intervals. In all, 52 million years (m.y.) of time and 7700 ft. of beds, marine shales and continental sandstones, are involved (150 ft./m.y. or 1 ft. in 7000 years). The sedimentation rate for the three segments is constant within 10 per cent. For comparison Holmes (1945) cites a rate of sedimentation of 1 ft./7500 years for the Paleozoic Appalachian geosyncline and Umbgrove (1950) a rate of 1 ft./8000 years for the North Sea basin filled with 25,000 to 30,000 ft. of Mesozoic and Cenozoic sediments.

Dallmus (1958) has presented a stimulating study of the mechanics of basin evolution; by his definitions the Alberta and Peace River basins would be primary basins formed by subsidence of a portion of the earth's crust and related to the type Williston basin.

It is interesting that, for basinal sedimentation, the short term rate (for a period of 50 m.y.) is similar to the long term rate (using 250 m.y.).

This 150 ft./m.y. rate of basinal sedimentation is, of course, much less than the maximum observed rate for the Cretaceous; Holmes (1947) indicates that this may be between 800 and 1000 ft./m.y. Westward into the mountains in Alberta, Cretaceous sections thicken and short-term rate of sedimentation increases. This may be transition from basin to trough (Harrington, 1958), and the line of transition in Alberta and British Columbia would be marked by the present mountain front.

Twenhofel (1936) concludes that estimates of time based on thickness of strata "are hardly worth the paper they are written on." Certainly a rate of 1 ft. of sediment in 7500 years implies tissue-paper thin annual rates of sedimentation or that each of our sedimentary sections with its apparently conformable sequence of sediments hides a host of minor disconformities. Comparable (1 ft./2000 yr.) rates of sedimentation have been measured in the varved Green River shales (Knopf, 1957). It is perhaps pertinent that the Green River oil shales basin and the Cretaceous Clearwater sea basin received organic rich shales responsible for two of North America's largest unexploited hydrocarbon reserves, the Eocene oil shales and the MacMurray bituminous sands.

Hawkes (1958) concludes his 150th anniversary address for the Geological Society of London with a 50-year forecast: "... I venture to predict that they will then find Lyellian uniformitarianism to stand on an even broader and surer basis than it does today."

The uniform rates of sedimentation here reported lend certain support to such a view.

### *Conclusions*

Sanidine and biotite are equally argon retentive and give cogenetic "pairs" useful in K-Ar dating of volcanic rocks.

On the basis of K-Ar dates from 4 "pairs" and a biotite, it is believed that

middle Albian (Harmon) represents a time 116 m.y. ago; Cenomanian (Crownsnest) time was 95 m.y. ago; upper Campanian (Bearpaw) was 75 m.y. ago; and upper Maestrichtian (Kneehills) was 66 m.y. ago. By a limited extrapolation the Cretaceous period (Pembina) ended about 63 m.y. ago.

These dates are compatible with the paleogeography of western Canada and with measured intervals between dated bentonites.

Cretaceous basins marginal to the Cordilleran orogenic belts sagged at rates of 140 to 160 ft./m.y. from middle Albian to upper Maestrichtian time, and this rate remained constant although the type of sediment accumulating in the basin changed; sag mechanism appears to be controlled by very deep-seated epeirogenic processes.

Since bentonites are comparatively common throughout the Cretaceous and Tertiary of western North America, the conclusions suggested here are capable of more rigorous testing. These tests are in process.

### *Acknowledgments*

Most of the dating was done at the University of Alberta; however, initial work on the Crownsnest volcanics was done at the University of California, Berkeley, Calif. During the time of assembly of a mass spectrometer at the University of Alberta, runs were made on the University of Minnesota, Minneapolis, Minn. mass spectrometer. We are grateful to J. H. Reynolds of the University of California and to S. S. Goldich and A. O. Nier of the University of Minnesota for their cooperation. P. S. Warren and C. R. Stelck of the University of Alberta have contributed much information on Cretaceous stratigraphy and paleontology essential to the geologic control of the data presented. Alex Stelmach of the Rock Analysis laboratory at Alberta made the potassium analyses; Frank Dimitrov has drafted all illustrations. All this assistance is gratefully acknowledged.

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### *Discussion of the Paper*

J. L. KULP (*Lamont Geological Observatory, Columbia University, Palisades, N.Y.*): I call your attention to two new determinations made at the Lamont Laboratory on Mesozoic samples. First, there is a well-dated granite in Kelasury of the Georgian Soviet Socialist Republic studied by M. M. Rubinstein (discussed elsewhere in this monograph).

The geologic date of that is post-Bajocian, and it is certainly pre-Cretaceous. Rubinstein says that it is most likely Bathonian, which is the upper part of the Middle Jurassic. The age obtained was  $167 \pm 2$  m.y. using the decay constants  $\lambda_{\beta} = 4.72 \times 10^{-10} \text{ yr.}^{-1}$  and  $\lambda_{\alpha} = .584 \times 10^{-10} \text{ yr.}^{-1}$ .

In the Triassic, G. P. Erickson reports in this publication on biotite from the Palisades diabase that was almost surely intruded at the time of the basaltic flows of the east coast of the United States and would be intruded, therefore, somewhere in the upper Triassic. Presumably the intrusion took place toward the end of the Triassic simply because in New Jersey and Connecticut the flows are on the upper part of this depositional sequence; but no more certain statement can be made than that they are probably upper Triassic. The result is  $190 \pm 5$  m.y.

I wonder if G. H. Curtis would like to say anything about the Middle Cretaceous of the Coast Range of California that he dated.

G. H. CURTIS (*University of California, Berkeley, Calif.*): We published a report on this. I do not know that I want to say very much. Our tie-in with the stratigraphy is very poor. Our dates range from 84 to about 95 m.y. for rocks we think were intruded during Turonian-Cenomanian time, but we are not certain. They are certainly younger than Albian, and they are older than Santonian-Campanian, but that is as much as we can say about most of those that we have done.

I do have a date for the Pliensbachian below the Bajocian obtained from a granite from Alaska that is supposed to have a fairly good tie. It is probably pre-Pliensbachian.

L. T. SILVER (*California Institute of Technology, Pasadena, Calif.*): We have been doing some work in the Cretaceous sections of that particular type of tectonic belt that has just been described as being inappropriate for age dating; therefore, perhaps I should be hesitant about putting this age forward. This work consists of a study of the stratigraphic relationships of the peninsular batholith, which is undoubtedly correlative with the Southern California batholith.

We have a concordant U, Th-Pb age date of 116 m.y. on monazite that can be said to put a limiting age on the prebatholithic section here shown to be upper Albian by a very excellent fossil assemblage and to be older than lowermost Maestrichtian or uppermost Campanian.

In putting this forward I say that this number falls in that interval, but I have no idea just where.

I think we can say with a great deal of confidence that the upper Albian is older than 116 m.y. from the stratigraphic relationships here. Accordingly I am concerned about the fact that many of the dates communicated thus far do not seem to me to indicate the degree to which they limit stratigraphic ages, although that is what they do in general. There is a certain amount of looseness involved, particularly in the correlation of the stratigraphy, and I do not see that the numbers we have discussed indicate the limits with which correlation can be accomplished.

I think, for example, Curtis just now did make clear that what he was saying was a limiting number; but many of these other numbers do not indicate limits.

We have to be very careful for this reason. It is quite possible that each of these intervals in this column is equivalent to major intervals such as Pliocene, Miocene, Oligocene, and Eocene. As our present Holmes' subdivision is concerned, we assign just about as much time to the Cretaceous as we do to the entire Cenozoic. Simply calling something Albian is not sufficient. I might say that, in the time between the accumulation of the Middle and Upper Albian Section that is probably 20,000 feet or more in thickness in Baja California and the time of the development of the monazite (from which I provide this date), there was a major deformation and emplacement of a batholith; I just do not know what the time interval for this sort of thing is. This is one of the profits we shall eventually get from the age dating.

KULP: I think Silver has touched on a particularly important point that we should emphasize to our geological colleagues here.

As you can see, the methods have reached the state where, under reasonably ideal conditions, quantitative measurements can be made and in many of these cases actually define time of crystallization event within relatively narrow limits, but the number of places in the world where a stratigraphically well-defined event has occurred that can be dated in this way are few. One of the best situations that has been presented here is the dating of ash falls or flows intercalated in fossiliferous horizons. Too often the datable granites may cut

a certain fossiliferous horizon, but the upper limit may be unknown. One of the merits of this Kelasury granite and of one or two of these others that have been mentioned is that it cuts a fossiliferous horizon that can be defined and then is overlain by another fossiliferous horizon only slightly younger. The definition of the geological time scale is becoming more of a geological problem, and it will be necessary to use the whole globe as a sampling area in order to obtain the necessary critical points.

R. K. WANLESS (*Geological Survey of Canada, Ottawa, Ontario, Canada*): May I ask Folinsbee the significance of these slightly higher constants used at the University of Alberta. We are trying to pin these things down very closely. Elsewhere in this monograph are papers on methodology, but we have not got down to trying to use the same constants throughout.

As regards 5 per cent differences: some are involved in the constants when results from one laboratory are compared to those from another. I know we cannot be dictatorial about these things, but perhaps some sort of an agreement might be made whereby all the laboratories use the same constants so that when people pick up these values in the literature, they will know that they are calculated on the same basis and that any differences are either in laboratory work or in the correlation of data in the field. The results may not differ very much but most people, including ourselves, are using 0.585 and 4.72. Should we agree on one set of values?

KULP: The Committee on Age Work in the Soviet Union solved it by adopting arbitrary constants that, in so far as I can determine, are not based on any physically determined constant. Where superior physically determined constants are available I think they should be used, but individual judgment enters into the estimate of the quality of the measurement. Since enough work has not been done to make us unanimous on these matters I rather feel that we can put in our papers only what we use and let the geologists recalculate the ages if necessary. I think we still need a little freedom in this matter.

G. W. WETHERILL (*Carnegie Institution of Washington, Washington, D.C.*): I think it is confusing to keep changing these constants all the time, and I think it may well be that, as a result of future work of the sort that L. E. Glendenin reports elsewhere in this monograph, this value of 0.585, which we and many others have been using, might well be improved.

However, I think at the present time I shall continue to use this value. The question of rubidium is a somewhat different one because until fairly recently, within the last several years at any rate, there was no obvious advantage in using the laboratory measurements over the use of geological measurements.

I think this will have to be reconsidered. We ourselves have still been using the value:  $\lambda = 1.39 \times 10^{-11} \text{ yr.}^{-1}$ . However, I think a very good case might be made for using:  $\lambda = 1.47 \times 10^{-11} \text{ yr.}^{-1}$ ; but if one half of the people use one, and one half of the people use the other, the situation I think will be somewhat confusing.

Another point in connection with what Folinsbee was saying is that an additional source of confusion can arise if different values are used for the abundance of  $\text{K}^{40}$  and  $\text{Rb}^{87}$ . In connection with this, may I again make a point I have made previously: that as long as the same values are used for an  $\text{Rb}^{87}$

abundance and for the  $K^{40}$  abundance that are used by the people who did the absolute counting of natural potassium or for the gamma ray of natural rubidium, no error is introduced. It is erroneous to change the isotopic abundance without making a corresponding change in the decay constant. Actually, you did make a corresponding change in the decay constant, but this is another variable that is really unnecessary because it does not actually enter into the error in the ages at all: it cancels out.

S. S. GOLDICH (*United States Geological Survey, Washington, D.C.*): A number of years ago Nier determined the abundance of the potassium isotopes, and since then a number of other laboratories have done the same thing. He felt that the more recent determinations were certainly as good as his work, which he thought was not better than 1 per cent at best. Nier, therefore, decided to accept an average of the data for the relative abundance of  $K^{40}$ .

If you go all the way back, as Wetherill mentioned, you see that the numbers cancel out, and the fact that our constants are a little different does not affect the age at all. We believe very strongly that, in a good analytical approach to any problem, you do not standardize on the materials you are trying to measure and, therefore, we prefer to use the laboratory-determined constants. We think that the value of 47 billion years for the half life of  $Rb^{87}$  is the best available now but if someone comes up with a better value, we think that we should like to adopt it.

We find that the Soviets are using different constants, and the only difficulty is that it is difficult for me to figure out from the text just what constants they are using. Gerling's old constants (K-Ar) were geologically determined, and I must say that I think he did a good job. Maybe he should determine the rubidium constant geologically.

KULP: The constants the Soviets have been using the last year and one half for potassium have been  $\lambda_\beta = 4.9 \times 10^{-10} \text{ yr.}^{-1}$  and  $\lambda_e = 0.602 \times 10^{-10} \text{ yr.}^{-1}$ .

L. F. HERZOG (*The Pennsylvania State University, University Park, Pa.*): It seems to me if we make any agreement at all here that it should be to put more raw data in our papers, to put the ratios of daughter to parent as well as "ages" in our papers. Then there would be no confusion about the constant used.

This confusion has given trouble also in interpreting Soviet work; it has been difficult to know what constant they use; at least I found it hard until you just said what you said, namely that they all use the same value. I wish they would put their data in more often, then you could better evaluate what they are doing. I think we should all do this and also encourage new people in the field to do it. Then you can always get the new numbers out whenever somebody establishes a better half life.

WANLESS: I do not wish to belabor this point and I do not wish to have things dictated from a high authority, but it does seem to me that if, eventually, we are going to get these dates on IBM cards so that they can be used on a nation-wide or a continent-wide basis it will be very confusing if, every time you pick out one of these cards, you have to recalculate the age by using new constants to bring it up to date.

KULP: Actually the changes have not been too rapid recently. I think most



laboratories have been using similar constants; the only new thing that has come in, of course, is the Glendenin determination, and probably this will be used. I think if you compare the K-Ar with the Rb-Sr determinations on all pegmatites for which there are concordant U-Pb ages there is very good agreement between these ages, within 2 per cent using the  $4.7 \times 10^{10}$  yr. for the Rb<sup>87</sup> half life.

H. FAUL (*United States Geological Survey, Washington, D.C.*): I wish to support Wanless and to oppose Wasserburg, as I have done on occasion. It is very easy to tell the geologist to recompute it. Allow me to suggest that few geologists are prepared to make these calculations. They take the numbers as they are printed and use them that way.

L. E. GLENDENIN (*Argonne National Laboratory, Lemont, Ill.*): May I say that we are putting a lot of work into trying to sharpen up these decay constants. I think that they are nuclear properties and, therefore, should be measured in the laboratory and then applied in other fields. I promise that we shall continue to make a major effort to try to clean up the rest of the K<sup>40</sup> decay scheme. An item I neglected to mention earlier is that we have made one preliminary measurement of the gamma decay branch in K<sup>40</sup>. We obtained 3.0  $\mu\text{g./sec./gm.}$  of natural potassium. This is to be compared with the value of 3.4 selected from the literature by Aldrich and Wetherill. That is a considerable difference, and we shall certainly pursue this matter further. As I mentioned yesterday, we have an enriched K<sup>40</sup> source to use in this problem. Perhaps eventually K<sup>40</sup> will be in as good shape as we think the simpler case of Rb<sup>87</sup> is now.

WASSERBURG: Regarding the establishment of a convention on decay constants: for potassium it appears as if we are talking about approximately 2 per cent. Considering the present state of the technique, it is pointless to play games with this. It will appear with a decay constant convention as if the results were absolute.

We are now in real danger with those people who read only the numbers in a paper and treat them as "ages" instead of "dates." It is always necessary for people to read the papers and find out what was done and how the investigators evaluated their results. On occasion, I am tempted to present my data as the inverse hyperbolic tangent of the parent-daughter ratio instead of as "dates."



## SOME CRITICAL POINTS OF THE POST-CRYPTOZOIC GEOLOGICAL TIME SCALE

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Critical revision of the geological time scale necessitated by the intensive development of the K-Ar method requires due attention to the search for a sufficient number of critical points that are well-dated stratigraphically. With such points it becomes possible to diminish the necessity of interpolation between critical points by the thickness method.

It is generally known that of all the potassium minerals micas retain radiogenic argon best at low temperature. The loss of argon by mica, except for infrequent anomalous cases, evidently is insignificant and more or less constant; so much so that micas must be used as the principal material for getting critical points of the time scale by the K-Ar method. Mica is generally obtainable from granitic intrusives as well as from certain effusives. Intrusives that are sharply delineated stratigraphically are rare and irregularly distributed in time.

Great difficulties arise in finding suitable stratified mica-bearing effusives in which the micas are unaltered.

It becomes evident that at present we sometimes face the necessity of using less valuable data, that is, on the one hand determination of the age of micas from the intrusives with only one known age limit and, on the other hand, data on the K-feldspars, magmatic rocks samples, and glauconites. As the K-feldspars (apparently except for the varieties that have not undergone monoclinic-triclinic inversion, namely, sanidines<sup>1</sup>) in most cases lose part of their argon (generally 10 to 40 per cent), it is clear that obtained data can be used only as indicators of minimal age (upper limit) for corresponding parts of stratigraphical scale. This refers also to the magmatic rock samples, the necessary condition being absence of relics capable of carrying residual argon.

No less care is necessary while using data on glauconites. Along with authentic facts of loss of a part of radiogenic argon by glauconites (10 per cent at best) there are frequent cases of contamination of these authigenic minerals by older terrigenous material; for that reason, we often get anomalously high figures.

Let us now consider some of the data that, in my opinion, may be used for the geological time scale.

The territory of Georgia and of Caucasus in the Soviet Union have been investigated by geologists in detail, and they offer a choice of several critical points. Jurassic intrusives will be considered first. Within the area of development of Bajocian porphyritic series in western Georgia, several granitoid intrusives are known, cutting the Bajocian as well as older formations and covered by the transgressive Lower Cretaceous. The Bajocian age of the Porphyritic series is closely defined by a fauna of the uppermost zone (*Garantia garantiana*) of this stage found in the upper part of the series composed of tuffs, tuffaceous sandstones and argillites and, less frequently, tuff breccias. There are faunal proofs of the existence of two lower zones also and,

as for the lowermost zone, it must be present in those places where the Porphyritic series conformably follows the deposits of the upper Lias.<sup>2</sup>

One of the intrusives of western Georgia that cuts the Bajocian porphyritic series and the sandstone shaly deposits of Lias (forming a distinct contact halo of quartz-micaceous hornstones) is Kelasury intrusive, cropping out in the middle parts of the rivers Kelasury and Amtkhely over an area of 100 km.<sup>2</sup> Kelasury intrusive is formed of biotite and biotite-hornblende granites, aplitic and alaskitic granites, and granite porphyries. Less acid facies of granitoids with numerous xenoliths of neighboring rocks are developed in the peripheral parts of the intrusive. The southern part of the Kelasury intrusive is transgressively covered by the Lower Neocomian, which begins with a basal formation followed by schistose limestones dated paleontologically. Considering that G. Tschkhotua has discovered pebbles of this intrusive in the variegated series of Kimmeridgian-Tithonian (?) somewhat to the west and taking into account the fundamental importance of the Bathonian tectonic phase in the tectonic development of Transcaucasia established by A. Djanelidze,<sup>3</sup> I conclude, together with G. Tschkhotua and G. Zaridze, that this intrusive is Bathonian.<sup>4</sup> We took from the central part of the intrusive a monomineral fraction of nonchloritized biotite represented by comparatively large crystals (0.5 to 1 mm.). The age of this biotite was found to be  $167 \pm 9$  million years (m.y.) as indicated in TABLE 1.\* Individual measurements of the argon and potassium content in our sample were done also by J. L. Kulp, his figures (5.99 per cent K and .0416 mm.<sup>3</sup> s.t.p. Ar<sup>40</sup>/g) corresponding to an age of  $174 \pm 4$  m.y. (personal communication). Considering that these measurements were done in different laboratories by different methods, it is seen that the results are in excellent agreement.

With the purpose of eliminating the possibility (although less probable) that the Kelasury biotite is anomalous because our figure largely disagrees with the data on the length of the Jurassic period formerly acknowledged, we have also determined the age of biotite from the Gumysta granite. This intrusive, which cuts the sandstone-shaly series of the Triassic, is situated somewhat to the west of the Kelasury intrusive. The age of biotite was found to be  $174 \pm 8$  m.y.

Finally, we have investigated the Khevy (Khevis-Jvary) intrusive situated within the limits of the Dziroula massif that outcrops over an area of 60 km.<sup>2</sup> This intrusive cuts both the Paleozoic rocks and the Bajocian porphyritic series and is transgressively covered by the Neocomian.<sup>4</sup> Both age limits of this intrusive are in full analogy with the age limits of the Kelasury intrusive. The composition of the Khevy intrusive is generally quartz-dioritic. The main femic component is hornblende, but some biotite is present. Due to the fact that it was found difficult to obtain a monomineral fraction of biotite from this rock, we used the hornblende-biotite fraction extracted by the magnetic and electrostatic separation for the age determination. The results of these measurements of three samples are given in TABLE 1.

\* Potassium determinations were made by the chloroplatinate and perchlorate methods as well as by flame photometry. The content of radiogenic argon was measured by the isotope dilution method using an atmospheric argon standard. We used the following decay constants of K<sup>40</sup>:  $\lambda_a = 0.557 \cdot 10^{-10} \text{ yr.}^{-1}$ ,  $\lambda_\beta = 4.72 \cdot 10^{-10} \text{ yr.}^{-1}$ ,  $K^{40} = 0.0122$  per cent. The figures of other investigators are recalculated after these constants.

TABLE 1

No.	Samples	Geological age	K (%)	$A_{\pm 0} \text{ mm}^3 \times 10^4$ (s.t.p./g)	Age (m.y.)
1	Biotite from the alkaline pegmatite, Vakis- jvary	Upper Eocene	$7.75 \pm 0.23$ (4)*	$109 \pm 11$ (4)	$37 \pm 4$
2	Biotite from the Kelsury intrusive	Bathonian	$6.175 \pm 0.051$ (8)	$410 \pm 16$ (6)	$167 \pm 9$
3	Biotite from the Gumysta granite	Bathonian	$5.82 \pm 0.18$ (2)	$404 \pm 8$ (4)	$174 \pm 8$
4	Hornblende-biotite fraction from the quartz diorite of Khevy intrusive (sample A, frac- tion 0.25 mm.)	Bathonian	$1.18 \pm 0.04$ (2)	$78.8 \pm 2.4$ (2)	$168 \pm 10$
5	Same as No. 4	Bathonian	$1.51 \pm 0.04$ (2)	$111.4 \pm 4.1$ (3)	$185 \pm 12$
6	(Sample B, fraction 0.5 mm.) Same as No. 4	Bathonian	$1.50 \pm 0.04$ (2)	$101.6 \pm 4.1$ (5)	$170 \pm 11$
7	(Sample C, fraction 0.25 mm.) Glauconite from the calcareous glauconite	Upper Aptian-Lower Albian	$4.43 \pm 0.13$ (2)	$178 \pm 2$ (3)	$103 \pm 4$
8	Glauconite from glauconitic sandstone of Tal- linn horizon	Upper part of Lower Ordovician; lower part of Mid-Ordovician	$6.46 \pm 0.04$ (3)	$1302 \pm 11$ (6)	$467 \pm 9$

\* The numbers in parentheses are the numbers of determinations.

Corresponding figures  $168 \pm 10$ ,  $170 \pm 11$ , and  $185 \pm 12$  m.y. do not contradict one another and are in good agreement with the data on the Kelasury and Gumysta granites. The analysis of all these figures bring us to the conclusion that most probably the significance of absolute age for the end of the Middle Jurassic must be 170 to 175 m.y. This result makes it possible to estimate the length of the Jurassic period more confidently now than formerly. It is known that A. Holmes, in accordance with his B-scale, estimated the beginning of the Jurassic period as 152 m.y. and the end as 127 m.y. The data on Nevadian granites, given by Curtis, *et al.*,<sup>5</sup> shows that the end of the Jurassic period must be dated as 140 to 145 m.y., approximately the same figure obtained from the data on glauconite of Volgian stage of the Russian platform, if the loss of its argon content is assumed to be 10 per cent.<sup>6</sup>

Thus the length of the Upper Jurassic alone corresponds to the figure given earlier for the whole of the Jurassic period. Thus far, since we do not have samples permitting a precise definition of the absolute age of the Lower Jurassic, it is necessary to resort to indirect considerations. In so far as we know, neither data nor thickness of corresponding deposits nor paleontological data give reason to assume that the length of the Upper Jurassic is greater than the summary length of both the Lower and Middle Jurassic. Therefore, the length of the Jurassic period, 50 to 60 m.y., does not seem to be exaggerated and, for the lower limit, the figure of 190 to 200 m.y. suggests itself, which is somewhat greater than the figure recently proposed by J. L. Kulp.<sup>7</sup> The question arises that in this case the length of the Triassic may be estimated too short if we take its beginning in accordance with J. L. Kulp's 230 m.y.<sup>7</sup> It is impossible to give a well-grounded answer to this question for want of sufficiently reliable critical points for the Triassic but, in any case, the lesser length of the Triassic in comparison with the Jurassic apparently does not disagree with geological facts.

We have not had the opportunity to measure the age of stratigraphically well-dated Cretaceous micas. Only the figure of  $103 \pm 4$  m.y. obtained for glauconite taken from the deposits transitional from the Upper Aptian to Lower Albian of the northern Caucasus should be mentioned. This figure is in good agreement with the data for glauconite of approximately the same age from northern Caucasus recently published by Polevaya *et al.*<sup>6</sup> It should be supposed that in these cases too some loss of argon has taken place. A good critical point for the Paleogene comes from the pegmatoid bodies of Vakis-Jvary (River Nataneby, Guria) associated with the intrusive of alkaline syenites, cutting volcanic-sedimentary deposits of the Middle Eocene, dated by the nummulitic fauna. The neighboring rocks have undergone contact influence of this intrusive, and in the intrusive itself contact phenomena are distinctly expressed.

Pre-Oligocene age of the Vakis-Jvary intrusive, as well as other intermediate intrusives of this part of the Ajara-Thriaethian folded system,<sup>8</sup> is considered to be fixed with certitude; therefore this intrusive is referred to by the investigators as either the uppermost part of the Middle Eocene or the Upper Eocene. We have measured the age of the big crystals of biotite from Vakis-Jvary pegmatoids. The results are given in TABLE 1 with some corrections concerning



the content of potassium in comparison with the data published earlier.<sup>9</sup> The age of biotite ( $37 \pm 4$  m.y.) is not in discrepancy with the time scales of Holmes and Kulp, but it does not eliminate the possibility of some corrections in the latter.

In connection with the measurements of the age of the glauconite from the Tallin horizon of Estonia, Union of Soviet Socialist Republics, it is necessary to dwell briefly on the dating of this part of the Lower Paleozoic. The age of carefully selected monomineral fraction of glauconite (0.25 to 0.5 mm.) was found to be  $467 \pm 9$  m.y. Plevaya *et al.* obtained similar figures, 466, 468, and 474 m.y., for glauconite from the same locality.<sup>6</sup> Taking into account the stratigraphic position of the investigated samples and possible loss of some part of radiogenic argon too, it may be concluded that the base of the Ordovician must be dated by a figure not less than 500 to 510 m.y., again in agreement with Kulp's time scale.

### Summary

Some critical points of the geological time scale have been obtained by the K-Ar method for micas of certain intrusive bodies, introduced between narrow stratigraphic limits, and also for micas of stratified effusives. In addition micas of intrusives are used, for which one of the stratigraphic boundaries is established with sufficient certainty. In case of necessity, minimum ages may be ascertained by using glauconites, uncontaminated by older terrigenous minerals and feldspar.

These samples are all from the Caucasus region. The biotite of the Kelasury granitoid intrusive of the Post-Bajocian and Pre-Cretaceous (Bathonian) age gave  $167 \pm 9$  m.y. The biotite of the dacites of Fakhralo of the Post-Turonian and Pre-Eocene age gave  $57 \pm 8$  m.y. The biotite of the Upper Eocene alkali pegmatites of Vakis-Djvary gave  $37 \pm 4$  m.y.

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# SOME PALEOZOIC DATES IN MAINE, WESTERN EUROPE, AND SOUTHERN UNITED STATES

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In Maine there are several very interesting granites. The most interesting to some of us in the Geological Survey and at the Massachusetts Institute of Technology, Cambridge, Mass., have a stratigraphic relationship that makes them suitable for geologic time points.

A group of granites south of Calais, France, all apparently contemporaneous, is overlain by sandstone of the Perry formation that has long ago been dated and is generally accepted as being of Late Devonian age on the basis of plant fossils. The granite actually in contact with the Perry abuts another granite somewhat different petrographically. The contact between the two is indefinite. It is presumed that the two are merely phases of the same rock. This second granite abuts a third, again slightly different petrographically and with a contact that is not seen. This latter granite metamorphosed sediments of latest Silurian age, Wenlock or lower Gedinnian perhaps according to Boucot (personal communication). The fossils are poorly preserved, but there is reasonable assurance that they are Late Silurian in age, although the exact stage is questionable (Faul, 1960).

All these rocks give ages around 405 million years (m.y.) as shown in FIGURE 1, and it is assumed that they are all part of one batholith that crystallized about 405 m.y. ago. This time was after the Late Silurian and before the Late Devonian, according to the fossil record.

The second group of ages on the map outlines a more recent event that occurred about 360 m.y. ago. This is a widespread group that represents either intrusion or metamorphism in different places. My associates and I are now studying the relations of this event to others and have collected samples from all the points marked by open circles on the map. This same number, incidentally, crops up repeatedly in the Appalachian chain.

South of Mt. Katahdin, Me., lies a small body of gabbro containing a small amount of biotite in places. This material gives a K-Ar age of 460 m.y. and presumably represents still another event in the evolution of the northern Appalachians. Thus far we have found this age nowhere else in the north, and one can only speculate about the nature of the event that produced it.

In Europe we have a number of ages that are concordant, Rb-Sr, K-Ar, using the Flynn-Glendenin constant. I spent a long time trying to figure out the constant 5 or 6 per cent difference between the Rb-Sr and K-Ar ages here, and then, at Pittsburgh, Pa., I found out about the secret that Glendenin had uncovered and everything suddenly became concordant.

The age is about 320 m.y. on four granites of the Vosges. The granites here metamorphosed Tournaisian rocks that are unconformably overlain by Viséan rocks. The relationship between the Viséan and the Tournaisian is clear. The relationship between the Viséan and the granite is less clear, I hasten to add. I have not been able to check the contact, but I hope to do that next

year. Nevertheless I think this is perhaps the best tie point we have for the Paleozoic time scale thus far. The stratigraphic bracket, at any rate, is tighter here than anywhere else I know.

In the Schwarzwald, in the West German Federal Republic, we have four samples stratigraphically less well tied down giving exactly the same age within experimental error. In the Massif Central in France we have one probably



FIGURE 1.

TABLE 1  
AGE MEASUREMENTS ON BENTONITES FROM TENNESSEE AND ALABAMA\*

Bentonite layer ("Hass bed") in the Chattanooga shale near Sligo Bridge, Tenn. K-Ar (biotite)	340 ± 7 m.y.
Bentonite layer in the Carters limestone, Stones River group (Middle Ordovician) from two deep mines near Bessemer, Ala. K-Ar (biotite, average of 2 samples, Pyne mine and Wenonah No. 8)	419 ± 5 m.y.
Rb-Sr (biotite, Wenonah No. 8, Tilton, new data)	450 ± 40 m.y.
U <sup>238</sup> -Pb <sup>206</sup> (zircon, Tilton, new data)	445 ± 10 m.y.
U <sup>235</sup> -Pb <sup>207</sup> (zircon, Tilton, new data)	455 ± 10 m.y.
Pb <sup>207</sup> -Pb <sup>206</sup> (zircon, Tilton, new data)	545 ± 45 m.y.

\* These results confirm the data of Adams *et al.* (1958) and Edwards *et al.* (1959).

Mississippian granite, also giving the same concordant K-Ar, Rb-Sr age of 320 m.y.

However not all "Hercynian" granites in Europe are 320 m.y. old. We have measured one at Baveno on Lago Maggiore in northern Italy at 270 m.y. with Rb-Sr and K-Ar concordant with the new half life (Jäger and Faul, 1959). It seems very likely that the meaning of the name "Hercynian" will undergo substantial change as a result of continuing age work in Europe.

Returning now to the United States, we have also made a few measurements on bentonites from the Middle Ordovician of Alabama and the Late Devonian of Tennessee, and we generally confirm the results of Adams *et al.* (1958). The biotite in bentonites shows K-Ar ages about 10 per cent younger than the Rb-Sr ages, and the Rb-Sr ages roughly agree with the  $U^{238}$ - $Pb^{206}$  ages of the zircon. The zircon ages, however, are discordant. The results are summarized in the accompanying TABLE 1. This pattern seems to be characteristic, and it is questionable whether the biotite lost argon, gained potassium, or the discrepancy has some other geologic meaning. At the moment I have no reason for preferring any of the three alternatives. We are trying to analyze the sanidine now and that may help.

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### Discussion of the Paper

M. KAY (*Columbia University, New York, N.Y.*): In western New Hampshire and Vermont there have been reported to be granites that are pre-Silurian. Do you know anything about those? There is also a granite there that is described by Billings and Cleaves (1933) to be Silurian. I wonder if you would tell me if you have determined the age?

FAUL: No, I am not aware of any pre-Silurian granites there. Hurley might know something about them.

P. M. HURLEY (*Massachusetts Institute of Technology, Cambridge, Mass.*): There is one in this area, but it shows a somewhat younger age.

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## SOME POINTS ON THE GEOLOGICAL TIME SCALE FROM NOVA SCOTIA AND NEW ENGLAND

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I propose to report on some work done on three localities. A description of most of this work has already been published; however, I present this report now in order to obtain criticisms of it or comments upon it.

The three areas are Nova Scotia, the Narragansett Basin in Rhode Island, and another area in the vicinity of Jackman, Maine, referred to by H. Faul elsewhere in this monograph. P. M. Hurley has done the field work in both Rhode Island and the Jackman, Me., area, and H. W. Fairbairn has worked in Nova Scotia. Questions concerning field relations may be referred to them. I have participated in the analytical work.

The rocks in the Narragansett Basin are dated by their fossils as Pennsylvanian in age. There seems to be little question about that. These sedimentary rocks are intruded by granitic bodies, which have contributed to the metamorphism of these rocks. We have dated these metamorphosed sediments and the igneous rocks that intrude them. On the basis of their stratigraphy and fossils, these intrusive rocks and their metamorphic mineral products are post-Pennsylvanian in age. Based chiefly on K-Ar age measurements, with confirming evidence from Rb-Sr measurements, the average age for these rocks is  $245 \pm 20$  million years (m.y.).

The Quincy granite underlies these Pennsylvanian rocks. It has in general been thought to be a late Paleozoic rock and has been correlated, I believe, on the basis of lithology and chemical composition with the Cape Ann granite of Massachusetts and the Conway granite of New Hampshire. Assuming the date of 178 m.y. to be a minimum age for the Conway granite, this age is considerably less than the 280 m.y. age for the Quincy granite (TABLE 1).

For the Quincy granite we had to make analysis of the whole rock by the K-Ar method, and I believe no Rb-Sr date exists for this rock. Our minimum age of 280 m.y. for the Quincy granite seems reasonable, since this rock underlies the Pennsylvanian sediments dated at about 245 m.y. The 170 m.y. date for the Conway granite, with the K-Ar and Rb-Sr dates agreeing within experimental error for this rock, is a Mesozoic date.

In TABLE 2 are some of the dates in the Narragansett Basin, averaging about 240 m.y. They include biotite concentrates from contact rock and intrusive sills. A Rb-Sr age of 246 m.y. tends to confirm the K-Ar ages. The Westerly granite is dated at 240 m.y. by the K-Ar method alone. Leonard Herzog and I formerly obtained a much lower Rb-Sr age. However, it was of such poor quality that it remained unpublished except in an annual report to the Atomic Energy Commission, Washington, D.C. That Rb-Sr measurement should be repeated.

In TABLE 3 are a series of analyses of the Rhode Island formation sedimentary rocks. They are whole rock analyses and biotite analyses. The average age is about 254 m.y., with one Rb-Sr date to support the argon dates.

The work of Quinn *et al.* (1957), yielding lead-alpha ages of 234 m.y. for

TABLE 1

QUINCY GRANITE FORMERLY CORRELATED WITH CONWAY GRANITE IN NEW HAMPSHIRE,  
MAKING THE LATTER PRE-PENNSYLVANIAN

Age Measurements Indicate that These Granites are not Contemporaneous

Sample No.	Locality and description	K(%)	$A^{40}/K^{40}$	Air correction (%)	K-Ar age (m.y.)
Pre-Pennsylvanian					
R-3821	Swingle quarry, Mass.; whole rock sample of Quincy granite;† minimum age only	3.45	0.0178	5	$280 \pm 15$
Unknown stratigraphic position					
B-3126B	Redstone, N.H.; biotite from Conway granite	6.67 6.73 Av. 6.70	0.0108	6	$178 \pm 8$
		Rb (ppm)    Sr (ppm) $Sr^{87}/Rb^{87}$			
B-3126B	Same as above	2016    14.9    1.36    0.00238			$161 \pm 9$

\* K-Ar ages on feldspars give minimum values only.

$K^{40}: \lambda_e = 0.558 \times 10^{-10} \text{ yr.}^{-1}$

$\lambda = 5.30 \times 10^{-10} \text{ yr.}^{-1}$

$Rb^{87}: \lambda = 1.47 \times 10^{-11} \text{ yr.}^{-1}$

† Riebeckite from the Quincy granite contained 0.10 per cent potassium, making it a possible but difficult sample for argon analysis.

TABLE 2

K-AR AND Rb-Sr AGES ON MINERALS ASSOCIATED WITH GRANITES THAT INTRUDE THE  
PENNSYLVANIAN SECTION SOUTH OF PROVIDENCE, R.I.

Sample No.	Locality and mineral	K(%)	$Ar^{40}/K^{40}$	Air correction (%)	K-Ar age (m.y.)
B-3815	West end of Jamestown Bridge; biotite in contact rock adjacent to granite	7.09 7.12 Av. 7.10	0.0148	3	$237 \pm 11$
B-3816	West end of Jamestown Bridge; biotite from granitic still in contact zone	6.88 6.96 Av. 6.92	0.0143	12	$230 \pm 11$
B-3814	Sullivan Quarry, Bradford, R.I.: biotite from Westerly granite	6.28 6.33 Av. 6.31	0.0150	7	$240 \pm 12$
B-3815A	Biotite reconcentrated from B03815 above	Rb (ppm)    Sr (ppm) $Sr^{87}/Rb^{87}$	0.838	0.00370	$246 \pm 13$
		898    16.7			

\* Radiogenic.



the Westerly and Narragansett Pier granites, 270 m.y. for the Quincy and Cowesett granites, and 306 m.y. for the Rhode Island gneisses.

TABLE 4 provides data on the stratigraphic section near Jackman, Me. Much of the paleontological work was done by Arthur Boucot of the Massa-

TABLE 3  
K-AR AND Rb-Sr AGES ON METAMORPHIC MINERALS AND ROCKS  
FROM THE RHODE ISLAND FORMATION

Ages Therefore are Post- or Late-Pennsylvanian. Samples are listed from East to West, Approaching the Intrusive Granite Contacts. Average Metamorphic Mineral Age: 254 m.y.

Sample No.	Locality and description	K(%)	A <sup>40</sup> */K <sup>40</sup>	Air correc- tion (%)	K-Ar age (m.y.)	
Rhode Island, R.I.						
R-3917	0.7 miles south of Portsmouth on Route 138; medium gray slate	3.87 3.95 Av. 3.91	0.0159	6	253 ± 13	
R-3920	1.5 miles north of Middletown, on Route 144; gray slate	2.78 2.86 Av. 2.82	0.0144	13	230 ± 12	
Conanticut Island, R.I.						
R-3818	Taylor Point, 1.2 miles north of Jamestown; white papery slate	3.99 4.07 Av. 4.03	0.0164 0.0166	2 2	260 ± 13 263 ± 13	
B-3817	East end Jamestown Bridge. Impure biotite concentrate from biotite-garnet schist	3.31 3.28 Av. 3.30	0.0174	8	275 ± 13	
B-3817A	Reconcentrated biotite from B-3817	6.46 6.41 Av. 6.43	0.0155	9	250 ± 12	
B-3817A	Reconcentrated biotite from B-3817	Rb (ppm)†	Sr (ppm)	Sr <sup>87</sup> * (ppm)	Sr <sup>87</sup> */Rb <sup>87</sup>	Rb-Sr (age, m.y.)
		666	14.9	0.682	0.00369	246 ± 16

\* Radiogenic.

† All values quoted in ppm are by weight.

chusetts Institute of Technology. On the basis of the fossil evidence, the Seboomook slate is of Lower Devonian age. TABLE 5 lists several age measurements on these rocks. These ages average about 360 m.y. They include measurements on an intrusive quartz monzonite, a cordierite hornfels containing spiriferoids of Oriskany age, the Seboomook slate whole rock, and a por-

phyritic quartz monzonite biotite concentrate. There is one confirming Rb-Sr age.

Lyons *et al.* (1957) published lead-alpha ages on zircons from a quartz monzonite in this area of about 320 m.y. However these samples are now believed to be from an area within the pre-Upper Silurian quartz monzonite. It would be instructive to confirm this age by lead-isotope measurements of the zircon on the possibility that they may have retained the true metamorphic age of these rocks.

There are concordant ages of about 365 m.y. on the Hog Island granite, Samples B-3609 and B-3640, which are in agreement with the K-Ar date obtained by Henry Faul on this rock (published in this monograph). There are

TABLE 4  
STRATIGRAPHIC SECTION AND IMPORTANT FOSSILS NEAR JACKMAN, MAINE

Post-Oriskany Lower Devonian	Biotite quartz monzonite and bordering contact-metamorphic rocks Seboomook slate of Perkins (1925)	<i>Leptocoelia flabellites</i> , about three-fourths of one mile north of the contact with the stock. Spiriferoids of Oriskany type in the cordierite hornfels
Upper Silurian	Calcareous slate, argillaceous and sandy limestone, conglomerate, and calcareous sandstone	Brachiopods <i>Protathyris</i> sp. and <i>Chonetes jerseyensis</i> , near Fox's Camp, about 4 miles west-northwest of the contact with the stock. Less diagnostic brachiopods of Silurian age, near Mud Pond, about 0.9 of one mile west of contact with stock
Pre-Upper Silurian	Porphyritic quartz monzonite with coarse metacysts of K feldspar. Hornblende and biotite are extensively altered to chlorite, clinozoisite, and other minerals; plagioclase somewhat altered to white mica and clinozoisite	

also whole rock analyses of the Seboomook slate and adjacent rocks. I think it is especially noteworthy that these whole rock argon analyses give dates the same as those made on the biotite concentrates on rocks in the area.

The third area on which I wish to comment is Nova Scotia, where we have dated a number of intrusive granites. These granites intrude lower Devonian sediments. Their K-Ar and Sr-Rb average about 360 m.y. with a fairly high degree of concordancy between the argon and strontium ages. This work was recently published by Fairbairn *et al.* in 1960. In conclusion, I feel that on the basis of these measurements from Maine and Nova Scotia we can tentatively assign a date of 360 m.y. for the post-Lower Devonian metamorphism. On the basis of the age measurements on the Rhode Island rocks, we can tentatively assign a date of 245 m.y. for the post-Pennsylvanian metamorphism. I believe that plus or minus 20 m.y. would be a reasonable error to assign these dates.

TABLE 5

K-AR AND RB-SR AGES SHOWING MINIMUM AGE OF LOWER DEVONIAN IN SECTION NEAR JACKMAN, MAINE

Samples with Prefix R are Whole Rocks Analyzed at Massachusetts Institute of Technology,  
 Those with Prefix B are Biotites Analyzed at Massachusetts Institute of Technology,  
 and Those with Prefix Me. are Biotites Analyzed by the United States Geological  
 Survey by H. Faul

Sample No.	Locality	K (%)	Ar <sup>40</sup> /K <sup>40</sup>	Air correction (%)	Age (m.y.)	
B-3609	Quartz monzonite, southwest corner of Hog Island, Wood Pond, Attean quadrangle, Maine. 45°37.45'N., 70°16.95'W.	5.49	0.0231	16.0	360 ± 17	
		5.59	0.0239	5.5	370 ± 17	
		5.56	0.0233	0	362 ± 15	
		Av. 5.53			364 ± 15	
Me-10	Same as B-3609	7.01	0.0226	4.3	353 ± 10	
R-3883	Cordierite hornfels containing spiriferoids of Oriskany age, edge of Wood Pond, Jackman, Maine.	2.84	0.0243	0	365 ± 10	
		2.86				
		Av. 2.85				
R-3447	Seboomook slate, <sup>13</sup> 4.5 miles northwest of Jackman, on Route 201, Attean quadrangle. 45°41.48'N., 70°16.95'W.	2.61	0.0244	3.0	377 ± 18	
		2.71				
		Av. 2.66				
R-3444	Seboomook slate, Route 201 at Jackman Field, 2 miles north of Parlin Pond, Long Pond quadrangle. 45°33.18'N., 70°7.56'W.	3.29	0.0238	1.8	368 ± 15	
		3.26				
		Av. 3.27				
R-3448	Gray Seboomook slate, Route 15, 5 miles east of Jackman, west end of Long Pond, Long Pond quadrangle. 45°37.58'N., 70°9.63'W.	2.57	0.0224	12	350 ± 15	
		2.57				
		Av. 2.57				
B-3593	Porphyritic quartz monzonite, much chloritized, small island in Attean Pond, Attean quadrangle. 45°33.85'N., 70°18.60'W.	3.74	0.0229	3.2	356 ± 15	
Me-9	Two separate biotite concentrates from same location as B-3593	4.47	0.0236	17	366 ± 10	
		4.01	0.0236	32	366 ± 10	
Sample No.	Locality	Sr (ppm)	Rb (ppm)	Sr <sup>87</sup> * (ppm)	Sr <sup>87</sup> * Rb <sup>87</sup>	Rb-Sr age
B-3609A	Same as B-3609, except purer biotite concentrate	46.1	472	0.720	0.00538	366 ± 28

\* Radiogenic.

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# SOME CRITICAL POINTS FOR THE PALEOZOIC TIME SCALE FROM THE BRITISH ISLES

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## *Introduction*

This work began as an investigation into the ages of British granites, the first results (K-Ar ages by the total volume method) being reported by Mayne *et al.*<sup>1</sup> in support of their proposed extension of the geological time scale. The length of this extension was subsequently criticized on general grounds,<sup>2,3</sup> and independent redeterminations of the age of micas from these intrusions by the K-Ar and Rb-Sr methods<sup>4</sup> confirm the finding that the values obtained by Mayne for the Caledonian granites are probably too high.

This paper reviews the geology of certain British Caledonian and Hercynian intrusives proposed as reference points for an absolute geological time-scale and reports some new age data obtained by A. A. Mills and H. Faul.

## *The Caledonian Intrusives*

The term Caledonian is used here to indicate igneous rocks formed in the pre-Upper Devonian orogenies affecting most of Scotland and adjoining areas. In this group are the Shap and Creetown "granites," which cut folded Ordovician-Silurian series in the Lake District of northwest England and south Scotland respectively. A generalized map is shown in FIGURE 1.

In south Scotland the folding is of post-Wenlockian age, but Ludlovian (highest Silurian) strata are folded in the Lake District. The eastern part of the Lower Paleozoic belt of south Scotland is unconformably overlain by fossiliferous Lower Devonian strata, but in the area of the map the "Lower Devonian" is unfossiliferous.

The Shap adamellite cuts Ordovician strata,<sup>5</sup> but its metamorphic aureole affects the Silurian and the associated radial dyke swarm cuts the Ludlovian. Pebbles of Shap adamellite are found in the overlying Lower Carboniferous<sup>6</sup> that, together with conformable underlying Upper Devonian, covers the folded Lower Paleozoics.

The Creetown granite (erroneously listed as "Cairnsmore of Fleet" in Mayne *et al.*)<sup>1</sup> cuts Lower Silurian strata and the Leinster (Eire) granite the Ordovician, but both lie within the belt of post-Silurian folding.

Thus the interval Upper Silurian to Upper Devonian is available for these intrusions. A more precise assessment of stratigraphic age can be made by considering specific petrological and structural arguments. The dated intrusives are all members of the postorogenic calc-alkaline igneous suite of the Caledonides, which form a well-marked petrographic province.<sup>7</sup> This suite has volcanic members of proved Lower Devonian age, and the associated intrusives are generally believed to be contemporaneous (as at Glencoe in the Central

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Highlands of Scotland).<sup>8</sup> Igneous activity ceased before widespread folding and erosion antedating the Upper Devonian occurred. Middle Devonian strata are not recognized in the region described, the relevant successions being set out in TABLE 1.

The stratigraphic position of the Mell Fell Conglomerate (FIGURE 1 and TABLE 1) is of importance in deciding the age of the Shap intrusion. This coarse postorogenic conglomerate has suffered pre-Upper Devonian folding and is probably of Lower Devonian age.<sup>6</sup> It is thought to have been formed as a



FIGURE 1. A much generalized map of southwest Scotland and northwest England showing the positions of the Shap and Creetown intrusions.

result of earth movements associated with the folding of the Silurian and subsequent intrusion of the Shap adamellite.

It is therefore considered most probable that the Caledonian Shap, Creetown and Leinster granites were intruded in the early part of the interval Upper Silurian to Upper Devonian, antedating the widespread moderate folding and extensive erosion that affects the Lower Devonian. These intrusives are consequently assigned to Downtonian or Lower Old Red Sandstone times, which are the continental equivalents of the marine Lower Devonian. No visible alteration of these intrusions has occurred, with the exception of late-stage magmatic effects.<sup>9,10</sup> The ages obtained by K-Ar and Rb-Sr measurements on the micas of these rocks should therefore reflect the actual date of intrusion and crystallization of these bodies.

TABLE 1  
CONTINENTAL DEVONIAN SUCCESSIONS IN GREAT BRITAIN

South Wales	West Midlands	Northwest England	South Scotland Northeast England	Midland Valley of Scotland	Central Highlands
Carboniferous*		Carboniferous*	Carboniferous*	Carboniferous*	
Upper Devonian* Folding	Upper Devonian* Folding	Upper Devonian Extensive erosion Folding	Upper Devonian† Extensive erosion Folding	Upper Devonian† Extensive erosion Folding	
Lower Devonian†	Lower Devonian†	Mell Fell Conglomerate?	Lower Devonian with volcanics and in- trusives (such as Creetown)	Lower Devonian† with volcanics	Lower Devonian† with volcanics and in- trusives (Glencoe)
Downtonian†	Downtonian†	Shap Adamellite?		Downtonian† with vol- canics	
Upper Silurian*	Upper Silurian* (Ludlovian)	Upper Silurian* (Ludlovian)	Silurian* (Wenlock- ian)	Silurian* or L. Ordovi- cian*	Dalradian schists

\* Marine faunas.  
† Nonmarine faunas.

Age data obtained by various workers for micas separated from these rocks are assembled in TABLES 2 (Rb-Sr) and 3 (K-Ar). A slight increase in certain of the Rb-Sr figures above those quoted in Kulp *et al.*<sup>4</sup> is a result of recalibration of the spike solutions. The mean Rb-Sr age is  $400 \pm 10$  m.y., while the mean K-Ar age is  $390 \pm 10$  m.y. This agreement between ages determined from two independent decay schemes gives confidence<sup>11,12,13</sup> for considering a

TABLE 2  
RUBIDIUM-STRONTIUM AGES OF MICAS FROM CALEDONIAN INTRUSIVES  
( $T_{1/2} = 4.7 \times 10^{10}$  yrs.)

Rock unit and location	Mineral	Specimen no.	Analyst	Rubidium (ppm)	Normal strontium (ppm)	Radio-genic Sr <sup>87</sup> (ppm)	Apparent age (m.y.)
Shap adamellite	Biotite	7680	*	843	11.5	1.38	391 $\pm$ 15
				845	13.9	1.42	401 $\pm$ 15
Shap, Westmorland, England	Biotite	20405	*	794	10.0	1.34	403 $\pm$ 15
				802	11.4	1.32	394 $\pm$ 15
	Biotite	—	†	766	36.0	1.19	380 $\pm$ 19
				801	39.0	1.30	
				773	34.0	1.19	364 $\pm$ 24
				793	34.0	1.20	
Creetown granite Creetown, Kirkcudbrightshire, Scotland	Biotite	20501	*	532	23.5	0.87	388 $\pm$ 19
				518	23.4	0.89	410 $\pm$ 20
							Mean 399 $\pm$ 16
Leinster granite Dublin, Eire	Biotite	DB-1B	*	1064	28.7	1.78	400 $\pm$ 16
				1071	26.5	1.79	399 $\pm$ 16
	Muscovite	DB-1M	*	861	14.9	1.45	403 $\pm$ 15
				830	15.1	1.46	418 $\pm$ 16
							Mean 405 $\pm$ 12

\* A. A. Mills, Department of Geology and Mineralogy, University Museum, Oxford. Weighted mean of all analyses =  $400 \pm 10$ .

† R. K. Webster, Analytical Chemistry Branch, A.E.R.E., Harwell, Berks. The sample of separated biotite was less pure than that available to Mills.

mean age of 395 m.y. to be close to the absolute age of these Caledonian intrusives and, for the reasons stated above, this is thought to characterize an event within Lower Devonian time. On the Holmes Time Scale B<sup>14</sup> this interval is placed at about 300 to 313 m.y. ago.

### *The Hercynian Granites*

The southern part of England lies within the major east-west European orogenic belt generally known as the Variscides or Hercynian chain. Within

this region a major eugeosyncline developed during the Devonian and Carboniferous. In the later part of the Lower Carboniferous, the Upper Carboniferous and, possibly, the Permian, this area suffered folding, metamorphism, and major igneous intrusion.

The geological setting of the Dartmoor and Land's End granites is shown in FIGURE 2. The shale-greywacke-volcanic series is folded into a major east-west structure<sup>15</sup> in which Devonian to Lower Westphalian strata are preserved. Some of the highest beds contain *Alethopteris lonchitica* and *A. serli*,<sup>16</sup> *Gastrio-*

TABLE 3  
POTASSIUM-ARGON AGES OF MICAS FROM CALEDONIAN INTRUSIVES  
( $\lambda\beta = 4.72 \times 10^{-10}$ ,  $R = 0.124$ )

Rock unit and location	Mineral	Specimen no.	Sample weight (gm.)	Radio-genic* Ar <sup>40</sup> (ppm)	Atmos-pheric* Ar <sup>40</sup> (%)	Potas-sium† (%)	Apparent age (m.y.)	Mayne <i>et al.</i> <sup>1</sup> (recalculated)
Shap adamellite Shap, Westmor-land, England	Biotite	7680	2.568	0.198	9	6.36	393 ± 12	465-500
			2.505	0.196	3		391 ± 20	
	Biotite	20405	2.870	0.185	10	5.89	397 ± 12	
			2.429	0.178	15		383 ± 12	
			Weighted mean . . .				391 ± 7	
Creetown granite Creetown, Kirk-cudbrightshire, Scotland	Biotite	20501	1.488	0.215	8	6.97	390 ± 12	460
Leinster granite Dublin, Eire	Biotite	DB-1B	3.622	0.184	14	6.21	377 ± 11	—
			3.173	0.187	3		381 ± 11	
	Muscovite	DB-1M	2.836	0.258	7	8.32	392 ± 12	
			2.450	0.258	5		392 ± 12	
			Weighted mean . . .				386 ± 6	

\* All argon analyses by Long and Giffin.<sup>4</sup>

† All potassium analyses by Ledoux and Co., Teaneck, N.J.

*ceras* cf. *carbonarium*,<sup>17</sup> and lamellibranchs,<sup>18</sup> all indicative of the Lower Westphalian. The granites cut these folded strata, the Dartmoor granite being clearly later than the overfolding on east-west axes.<sup>19</sup> The adjacent sediments are contact metamorphosed and extensively mineralized.

A major belt of mineralization (the galenas of which yield a model age, Holmes-Houtermans, of 280 m.y.)<sup>20</sup> extends from the Dartmoor granite to Land's End, cutting obliquely across the fold structures (FIGURE 2). The stratigraphy of the Land's End granite shows only that it is post-Lower Devonian but, from its close mineralogical and chemical similarities with the Dartmoor and other granites in the region, it is generally thought to be contemporaneous with them.

These granites are therefore post-Lower Westphalian. Approximately 60

miles northeast of Dartmoor, however, lies a further group of Devonian-Carboniferous sediments (FIGURE 2). These sediments include coal measures of Lower Stephanian age<sup>21</sup> overfolded on east-west axes, the highest strata containing *Anthraconaia prolifera* and *Pecopteris spp.* The overfolding is of a type similar to that of Devon and is probably of the same age. There is therefore a strong probability that the Dartmoor (and Land's End) granites are post-Lower Stephanian.

The upper limit of stratigraphic position is provided by continental deposits conventionally referred to the Permian and Trias (FIGURE 2). The British Permo-Triassic deposits are largely unfossiliferous: the relevant data are summarized in TABLE 4. There is little reason why the Dartmoor granite

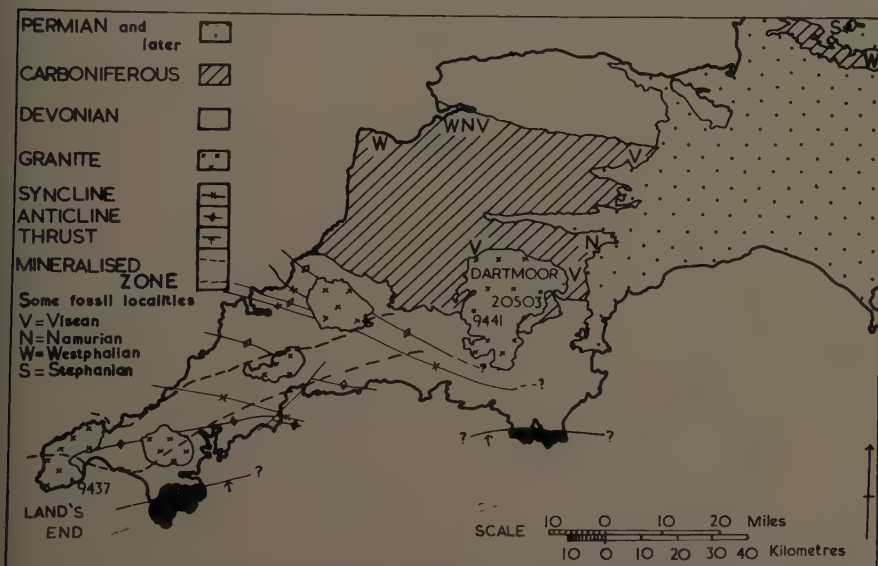


FIGURE 2. The geological setting of the Dartmoor and Land's End granites. Fold structures are based on Hendricks;<sup>15</sup> the generalized position of the mineralized zone is taken from Dewey.<sup>40</sup>

should not be of any Permian date; in general, however, earth movements seem to have been largely complete before the Upper Permian (Zechstein). Accordingly we conclude that the granites of southwest England were probably emplaced in the highest Carboniferous or early Permian times.

Age data for biotites separated from these granites are shown in TABLES 5 (Rb-Sr) and 6 (K-Ar). The mean Rb-Sr age is  $285 \pm 8$  m.y. The mean K-Ar ages obtained at Lamont<sup>4</sup> ( $271 \pm 5$  m.y.) and by Faul (personal communication) of 290 m.y. differ by a larger amount than that expected from the claimed experimental errors and should be compared with the age of 298 m.y. obtained by Mayne.<sup>1</sup>

A recent analysis<sup>22</sup> of a uraninite from the mineralized zone associated with, and younger than, the southwest England granites should also be considered. This contained 0.0026 per cent Pb<sup>204</sup> and gave a concordant age of 288 m.y.



TABLE 4  
PERMO-TRIASSIC SUCCESSIONS IN ENGLAND (MUCH GENERALIZED)

Southwest England (ca. 2000 ft.)	Southwest Midlands (3000 ft.)	North Midlands (2000-5000 ft.)	Northeast England (5000 ft.)	
Red sandstones	Red marls*	Red marls*	Red marls	Upper
Conglomerates	Red sandstones*	Red sandstones and conglomerates	Red sandstones and conglomerates	Middle
Marls	Conglomerates		Marine Limestone* (Upper Zechstein)	Lower
Volcanic series		Erosion Folding	Marl* (Lower Zechstein)	Upper
Clays	Erosion Folding	Autunian*?	Erosion Folding	Lower
Erosion Intrusion Folding	Lower Stephanian* Red beds	Stephanian* Upper Westphalian* Lower Westphalian* Coal measures	Upper Westphalian* Red beds Coal measures	PERMIAN
Lower Westphalian Culm*				CARBONIFEROUS

\* Fossiliferous.

TABLE 5  
RUBIDIUM-STRONTIUM AGES OF BIOTITES FROM HERCYNIAN INTRUSIVES  
( $T_{1/2} = 4.7 \times 10^{10}$  yrs.)

Rock unit and location	Specimen no.	Analyst	Rubidium (ppm)	Normal strontium (ppm)	Radiogenic $Sr^{87}$ (ppm)	Apparent age (m.y.)
Dartmoor granite Haytor Rocks, Devonshire, Eng- land	20503	*	1289	9.91	1.48	275 $\pm$ 10
			1276	9.65	1.53	287 $\pm$ 10
			1279	9.58	1.53	286 $\pm$ 10
			1280	—	—	—
	20503	†	1278	25.0	1.56	292 $\pm$ 12
						Mean 285 $\pm$ 8
Land's End granite Botallack Cove, Corn- wall, England	9437	*	1963	11.8	2.22	270 $\pm$ 9

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† B. J. Giletti, Department of Geology and Mineralogy, University Museum, Oxford.

TABLE 6  
POTASSIUM-ARGON AGES OF BIOTITE FROM HEYRCYNIAN INTRUSIVES  
( $\lambda_{\beta} = 4.72 \times 10^{-10}$ ,  $R = 0.124$ )

Rock unit and location	Specimen no.	Sample weight (gm.)	Radio- genic $Ar^{40}$ (%)	Atmos- pheric $Ar^{40}$ (%)	Potas- sium (%)	Apparent age (m.y.)	Analyst		Mayne <i>et al.</i> <sup>1</sup> (recal- culated) m.y.
							Argon	Potas- sium	
Dartmoor granite Haytor Rocks, Devon- shire, Eng- land	20503 (i)	2.388	0.148	34	6.93	279 $\pm$ 8	*	†	298
		2.083	0.132	6	6.57	263 $\pm$ 13	*	†	
	20503 (ii)	3.577	0.150	2	7.22	271 $\pm$ 8	*	†	
		3.072	0.148	9		269 $\pm$ 8	*	†	
			Weighted mean . . . .					271 $\pm$ 5	
	20503 (i)	—	0.159	49	7.05	292	§		
		—	0.157	14		289	§		
			Mean . . . . .					290	
Land's End granite Botallack Cove, Cornwall, England	9437	1.883	0.134	10	7.17	250 $\pm$ 15	*	†	330

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† C. McInnes, Dept. of Geology and Mineralogy, Oxford, England.

‡ Ledoux and Co., Teaneck, N.J.

§ H. Faul, United States Geological Survey, Washington, D.C.

|| W. W. Brannock, United States Geological Survey, Washington, D.C.

In view of the discrepancy between the K-Ar ages, it is considered that the mean Rb-Sr age of  $285 \pm 8$  m.y. gives the best estimate for the age of the Dartmoor granite and should be close to the absolute age of this intrusion. The Land's End granite could be contemporaneous within the limits of experimental error, but the available evidence seems to suggest that it may be somewhat younger.

It is therefore concluded that the Permo-Carboniferous boundary should be placed within the interval  $285 \pm 10$  m.y. ago. In Holmes' Scale B<sup>14</sup> this division is drawn at 203 m.y.

### *Experimental Methods*

The techniques employed by Long and Giffin to determine the age of these micas by the K-Ar method are described elsewhere.<sup>23</sup> The procedure used by Webster for radioactive age determination has also been published.<sup>24,25</sup>

The method of Rb-Sr age determination developed by Giletti and Mills at Oxford is basically similar to those described by earlier workers in this field,<sup>11, 13, 26, 27, 28</sup> isotope dilution techniques<sup>29</sup> being used throughout. Details will be published elsewhere (B. J. Giletti, personal communication).

Minerals were isolated with the Frantz Isodynamic Separator, purity being controlled microscopically by counting particles in random fields. All those micas analyzed by one of us (A.A.M.) for the present study were better than 98 per cent pure, except for the Leinster biotite that was intimately chloritized. Separated minerals were submitted to optical spectrographic analysis for rubidium and strontium (A. A. Mills, personal communication), enabling their suitability for Rb-Sr dating to be assessed and optimum spike volumes calculated. Of the minerals contained in the intrusives discussed in this paper, only biotites (and, in the case of the Leinster granite, muscovite) proved usable: the associated feldspars contained too much common strontium.

Isotopically-enriched Rb<sup>87</sup> and Sr<sup>86</sup> spikes were obtained from Atomic Energy Research Establishment, Harwell, England. Both strontium and rubidium were determined on the same mineral sample to avoid weighing errors and possible variations in concentration.<sup>30</sup>

A Metropolitan-Vickers MS 5 solid source mass spectrometer was used for all isotopic analyses at Oxford. This instrument has a 90°, 12-inch radius analyser tube, and is equipped with an electron multiplier detector. A multiplier correction of (atomic weight ratio)<sup>1/2</sup> was applied to all ratios measured with this detector.<sup>31</sup> A single filament source was used for both rubidium and strontium with a fresh tantalum ribbon for each determination. Calibration, discrimination, and selective emission were checked with samples of normal rubidium and strontium.

The contribution of Sr<sup>87</sup> from strontium incorporated at the time of formation of the mineral was calculated by assuming that the isotopic composition of this element did not then differ significantly from that of present-day common strontium.<sup>32</sup> A half life of  $4.7 \times 10^{10}$  years for Rb<sup>87</sup> was accepted.<sup>33</sup>

The errors given in the tables were derived from a consideration of inherent errors,<sup>13</sup> variation between replicates, and analysis of standards. The error at the 1  $\sigma$  level varies from 3 to 5 per cent for a single determination, depending upon the ratio of rubidium to common strontium in the sample.

*Results*

Both K-Ar and Rb-Sr ages indicate the Caledonian Shap and the Creetown and Leinster granites to be contemporaneous within the limits of experimental error. A mean age of 395 m.y. for these intrusions is assigned to the interval post-Upper Silurian to Middle Devonian, most probably applying to Lower Devonian time.

Agreement between all methods is less satisfactory for the Dartmoor granite, but 285 m.y. is thought to be close to the absolute age of this intrusion. The Land's End granite may be slightly younger. From the stratigraphy of these masses it is considered that the Permo-Carboniferous boundary should be placed within the interval  $285 \pm 10$  m.y. ago.

These results support recent suggestions<sup>1,34-39</sup> for lengthening the Holmes Time Scale,<sup>14</sup> but not to the extent originally proposed by Mayne *et al.*<sup>2</sup>

*Summary*

Age data obtained by the Rb-Sr and K-Ar methods have been presented for micas from intrusive rocks of the British Isles. A mean age of 395 m.y. is indicated for Caledonian intrusives of probable Late Devonian age and an age of 285 m.y. for Hercynian intrusives assignable to the highest Carboniferous or Late Permian.

*Acknowledgments*

We are grateful to all those who have contributed data and assisted in discussions, particularly B. J. Giletti and W. S. McKerrow of Oxford University. The mineral separations were largely carried out by C. McInnes and Jean Dunsdon of Oxford University. Thanks are due to the Director of the Geological Survey of Great Britain, for specimens of Creetown granite, and to J. L. Kulp, Columbia University, New York, N.Y., for the micas from the Leinster granite.

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*Discussion of the Paper*

M. H. DODSON AND D. YORK\* (*Department of Geology and Mineralogy, University of Oxford, Oxford, England*): Further potassium-argon measurements on the Shap and Dartmoor granites have recently been made at Oxford using both the "total volume" and the isotope-dilution techniques to determine the argon contents. The results of these measurements by both techniques agree within the limits of error with the potassium-argon ages given by Kulp *et al.*

The new measurements by the total-volume method used essentially the same extraction apparatus and the same techniques of gas purification as were employed by Mayne *et al.* The  $\text{Ar}^{36}/\text{Ar}^{40}$  ratios were determined on a new Reynolds-type mass spectrometer assembled by the authors. It is not certain what the source of error in the early measurements was, but it is possible that it was connected with the determination of the amount of atmospheric argon contamination.

Full details will be published elsewhere when the series of measurements is completed.

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## BENTONITES AS ABSOLUTE TIME-STRATIGRAPHIC CALIBRATION POINTS\*

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Bentonites or altered volcanic ashes have long been recognized as useful marker beds in certain stratigraphic sections. The thin and continuous bentonites represent one of the very few cases of complete coincidence between bedding planes and planes of the same geologic age. Thus, in favorable cases, the field relationships clearly require that a bed that can be traced scores of miles or a series of beds separated stratigraphically by only a few feet must have been deposited within a very short interval of geologic time. The occurrence of satisfactory index fossils under, over, and occasionally even in bentonite layers has established some bentonites as ideal relative time markers.

The direct and absolute dating of the time of deposition of a volcanic ash in the Paleozoic appears impossible. However, some altered volcanic ashes or bentonites contain datable minerals whose average time of crystallization is not likely to precede the time of ash deposition by a significant amount. This assumption regarding the insignificant difference between the times of crystal formation and ash deposition has been substantiated by experimental results. These experimental results also form a basis for judging the advantages and applicability of such results in dating the Middle Ordovician in particular and establishing a better geologic time scale in general.

Since 1956 nearly 200 bentonite or altered volcanic ash samples from the United States and Europe have been examined at The Rice Institute to determine their suitability for absolute age determinations. Suitability is a function of many factors including: (1) fresh and uncontaminated field sample; (2) the possibility of recovering a sample of biotite or sanidine of sufficient purity and amount for either Rb-Sr or K-Ar determinations or the possibility of recovering a sample of zircon, monazite, or apatite of sufficient purity and amount for U, Th, and Pb isotopic determinations; (3) the absence of garnet, kyanite, and other minerals that would be inconsistent with an uncontaminated pyroclastic origin; (4) the presence of euhedral zircon, biotite, apatite, or euhedral quartz with little or no prism development and an absence of rounding and overgrowths; and (5) zircons whose autoradiographs show an uniformly low alpha activity consistent with a pyroclastic and uniform source.

Preliminary isotopic Rb-Sr ages on biotites separated from the Middle Ordovician of the eastern United States (Adams *et al.*, 1958) were encouraging, and it was decided to concentrate on these bentonites because: (1) somewhat higher ages than those generally accepted in 1958 were indicated by the Rb-Sr ages; (2) it was known that several of these bentonites had sufficient zircon for U and Pb isotopic analysis; (3) the stratigraphy was relatively well worked out; and (4) these were the oldest available bentonites at that time and hence provided the best opportunity for obtaining the least ambiguous ages by all of the isotope methods in current use.

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$U^{238}$ - $Pb^{206}$  ages for three zircon and one combined zircon and monazite separates from the Middle Ordovician of eastern Tennessee have been reported elsewhere (Edwards *et al.*, 1959). In addition H. Faul and G. R. Tilton (personal communication) have determined isotopic U-Pb ages for one zircon and Rb-Sr and K-Ar ages for a biotite from a stratigraphically equivalent layer in Alabama. J. H. Reynolds (personal communication) has also made K-Ar age determinations on two Tennessee biotites separated at The Rice Institute. Although these studies are still in progress, 17 independent age determinations on minerals from bentonites in the Middle Ordovician of Tennessee and Alabama are available: five  $U^{238}$ - $Pb^{206}$ , five  $U^{235}$ - $Pb^{207}$ , four Rb-Sr, and three K-Ar. To these 17 independent age determinations also might be added five less certain  $Pb^{207}$ - $Pb^{206}$  ages (Adams *et al.*, in press).

There being no question that these minerals are from ash falls deposited during a very short interval in the Middle Ordovician, all of these 17 age determinations should be the same providing that: (1) the minerals analyzed crystallized an insignificantly short time before the ash fall; (2) the minerals have remained closed systems from the time of crystallization to the present; (3) there are no unusually large errors in either the isotopic or decay constant determinations; and (4) daughter products present at the time of crystallization do not necessitate either large or uncertain corrections. With these provisions and reservations in mind, the high precision of the 5  $U^{238}$ - $Pb^{206}$  ages is particularly noteworthy. These ages average 447 million years (m.y.) with all 5 figures within 9 m.y. or 2 per cent of the average. It should be noted that one of the samples yielding  $U^{238}$ - $Pb^{206}$  age of 446 m.y. might be given extra weight in the average because it had the smallest percentage of  $Pb^{204}$  and it was a mixture of zircon and monazite, with each mineral contributing about one half of the total alpha activity of the separate.

The  $U^{235}$ - $Pb^{207}$  ages are neither as precise nor as unambiguous as the  $U^{238}$ - $Pb^{206}$  ages. The percentage of  $Pb^{207}$  formed since crystallization is such that the  $Pb^{207}/Pb^{204}$  ratio assumed for the lead incorporated during crystallization greatly affects the age calculated. Thus assuming a  $Pb^{207}/Pb^{204}$  ratio of 15.675 for this lead in all five samples, the  $U^{235}$ - $Pb^{207}$  ages are all higher than the 447 m.y. average. If a ratio of 16.500 is assumed for all five samples, the  $U^{235}$ - $Pb^{207}$  ages average 449 m.y. with all five values agreeing to within 18 m.y. A number of elaborate, but not necessarily realistic, mathematical models can be applied to these data, particularly if the same lead reservoir for all samples is assumed. There is also the experimental possibility of determining the isotopic composition of the lead incorporated in the associated sanidine and of assuming that it represents the isotopic composition of the lead incorporated into the zircon at the time of crystallization. For the present summary it is sufficient to conclude that the  $U^{235}$ - $Pb^{207}$  ages do not necessarily disagree with the 447 m.y. average of the precise  $U^{238}$ - $Pb^{206}$  ages. Assuming the 447 m.y. age to be correct, the  $Pb^{207}/Pb^{204}$  ratios that must be used to calculate a concordant age are not extreme or unknown and merely mean that the lead incorporated during crystallization was not exactly the same in each sample and was not a homogeneous sample of terrestrial lead during the Middle Ordovician.

One of the four Rb-Sr biotite ages must be rejected as impossibly low. The other three have limits of error of  $\pm 40$  to 50 m.y. because of experimental

uncertainties. Within these limits the three Rb-Sr ages are consistent with the 447 m.y. figure obtained from the zircon separates. Two of the three K-Ar biotite ages are also impossibly low. These biotites were obtained from outcrop samples and were somewhat chloritized. H. Faul (personal communication) reports a K-Ar age of 420 m.y. for a fresh biotite sample obtained in a mine in Alabama. With the exception of this last figure, all of the 14 acceptable age calculations are considered to be consistent with the 447 m.y. average of the precise  $U^{238}$ - $Pb^{206}$  ages.

In evaluating the 447-m.y. figure for the age of the Middle Ordovician, the following points must be emphasized: (1) the high precision of the five  $U^{238}$ - $Pb^{206}$  ages is independent of ambiguous corrections; (2) four of the ages are based on isotopic data obtained at the Shell Development Laboratories, and the fifth age was determined completely independently at the Carnegie Institution of Washington, Washington, D.C.; and (3) these samples are Middle Ordovician; there are no ambiguities in the field relationships as is so commonly the case where sediments are dated by cross-cutting relationships with a datable granite. Current work is directed toward obtaining  $U^{238}$ - $Pb^{206}$  ages for zircons separated from Middle Ordovician bentonites in Scandinavia and west Texas. The west Texas samples have been assigned to both Trenton and Cincinnati, and it is just possible that this question in stratigraphy may be resolvable on the basis of  $U^{238}$ - $Pb^{206}$  dates. Sanidine coexistent with zircon is being separated for isotopic lead analysis to determine whether the lead is a so-called anomalous lead of the type required to make the  $U^{235}$ - $Pb^{207}$  age agree precisely with the  $U^{238}$ - $Pb^{206}$  age. In summary, there are many reasons to believe that a firm absolute date for the Middle Ordovician is very close to 447 m.y. It now appears that the error in this age will be 1 or 2 per cent (5 to 10 m.y.) and will represent any or all of the following variables: (1) variations between the time of crystallization of the zircons and their deposition in the ash fall; (2) very slight variations in stratigraphic position; (3) errors, particularly contamination, in the isotopic determinations; (4) uncertainties in the decay constant of  $U^{238}$ ; and (5) slight variations from sample to sample in the isotopic composition of the lead incorporated during crystallization.

It is not possible to determine at this time how useful bentonites will be for dating other geologic periods. Of the nearly 200 bentonites examined at The Rice Institute, only about 30 were found to contain a sufficient quantity of biotite or zircon for isotopic analysis. To date most of the bentonites did not contain a detectable concentration of either zircon or biotite. All three apatite separates from bentonites were so low in alpha activity that it was not feasible even to attempt an isotopic uranium and lead determination. From 20 to 80 or more kg. of bentonite are required to obtain zircon containing a minimum inventory of about 30  $\mu$ g. of lead. Most of the zircons found are only 20 to 40  $\mu$  long and, in addition to heavy liquids and magnetic separators, dielectric separators and continuous centrifuges in both water and air were found necessary to complete the separations. Despite these difficulties, datable bentonites in the Ordovician, Permian, Cretaceous, and Tertiary are known in Texas alone. A zircon concentrate has been obtained from a thin bentonite in the Chattanooga shale of Tennessee, which is very near the Mississippian-Devonian



period boundary. It must be considered a distinct possibility that datable bentonites or altered volcanic ashes can be found in fossiliferous sections of most, if not all, of the geologic periods. However, to locate these bentonites will require full cooperation between regional and field geologists in re-examining thin "clay partings" and "clay seams" to determine whether they are actually datable bentonites. In this connection, it should be noted that the presence of flakes of biotite can often be detected in the field with a hand lens and that such biotite is often a good indication of pyroclastic deposition.

If the present indications prove true, and if it is possible to match the precise and accurate stratigraphy of certain bentonites with precise and accurate age determinations to within about 1 per cent, then it will be possible to establish some excellent absolute time-stratigraphic calibration points in the geologic column. It would appear to be more accurate and useful to record the absolute age in terms of the local stratigraphy and fossil assemblages rather than extrapolating it to the beginning of a period. Thus the Stones River and Bays sediments of Tennessee and Alabama are believed to be  $447 \pm 10$  m.y. old, and all that can be said about an unconformity in some places marking the beginning of the Ordovician is that it is somewhat older.

### *Summary*

The unique position of bentonites as time-stratigraphic markers makes them ideally suitable for precise stratigraphic dating. Their wide distribution in rocks from the Ordovician to the present permits establishment of a time scale within the sedimentary record.

Bentonites contain several datable minerals. Biotite and sanidine are common and have yielded K-Ar or Rb-Sr dates. Biotite, however, is easily altered under most sedimentary conditions and may give unreliable and generally low dates. Sanidine is one of the more stable major minerals and merits extensive study. Zircon, although it is a very minor constituent, is the most stable datable mineral and is likely to remain a closed system during alteration of the volcanic ash. Of the various uranium-lead and thorium-lead dates which can be obtained from zircon,  $U^{238}$ - $Pb^{206}$  is the most reproducible and involves the fewest assumptions concerning the lead blank.

In dating zircons, 20 to 80 kg. of bentonite may be required. The large quantity is made necessary by the low concentration of zircons and the fact that extrusive zircons generally contain about one half as much thorium and uranium as intrusive zircons. Autoradiography has shown the presence of rare, highly radioactive grains (some of which are monazite) in the zircon separates, and a few per cent of these grains may account for 50 per cent of the total alpha activity. A number of autoradiographic, radiometric, chemical, and petrographic criteria have been developed to test the assumptions that the zircons are all pyroclastic and represent a closed system.

Thus far, five zircon dates from Middle Ordovician bentonites in the Eastern Interior Basin give an age of  $447 \pm 10$  m.y. The assumption that zircons in bentonites have crystallized only slightly before eruption can be tested by comparing dates from different areas, and for this purpose Middle Ordovician samples from west Texas and Sweden are being studied.



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## Discussion

J. L. KULP (*Lamont Geological Observatory, Columbia University, Palisades, N.Y.*): May I call your attention to five other dates before we begin our general discussion. N. I. Plevaya has done  $K^{40}$ - $Ca^{40}$  and  $K^{40}$ - $Ar^{40}$  determinations on sylvites by the isotope dilution method. She and her associates reported measurements on crystallized and recrystallized sylvite. On the sylvite designated unrecrystallized, they obtained concordant K-Ar and K-Ca ages. On the alleged recrystallized sylvite they obtained a K-Ca age equal to the K-Ca age on the unrecrystallized sylvite, but the K-Ar age on this was low. For Mid-Permian sylvite the age was  $240 \pm 5$  m.y.

Another Soviet determination that is relevant here is on a granite from Magnitogorsk that cuts lowermost Mississippian. The upper limit is not defined and the K-Ar age is 340 m.y., in good agreement with the result reported by H. Faul on the lowermost Mississippian bentonite.

My associates and I have obtained a sample of granite from east Greenland that intrudes fossiliferous lower Devonian and is overlain by fossiliferous Middle Devonian. We obtained an age of 390 m.y. by K-Ar on separated biotite.

Finally, I shall mention two of the U-Pb dates that are described by J. C. Cobb elsewhere in this monograph. They are minimum dates, one on the black shale from the Chattanooga giving 340 m.y. and 500 m.y. for the Upper Cambrian kolm of Sweden.

Are there any other dates that anyone wishes to add?

G. H. CURTIS (*University of California, Berkeley, Calif.*): My associates and I have dated two samples, both in duplicate from Australia: one from the Kuttung series that is not too well correlated with the world section other than being Upper Carboniferous and that is presumably best placed in the Pennsylvanian. The sample is from Lower Hunter Valley, New South Wales. It looks in thin section to be a welded tuff. It is an extremely dense rock and I suppose it could have been recrystallized, that is, the glassy ash could have been recrystallized, but it does look like a welded tuff. I did not collect this. Ted Irwin of the National University at Canberra collected the sample. The dating result is  $287 \pm 5$  m.y.

The other sample is from the very top of the Devonian (based on Devonian fish) from Snob's Creek, Warburton, Victoria, Australia. The result is  $344 \pm 5$  m.y.

P. M. HURLEY (*Massachusetts Institute of Technology, Cambridge, Mass.*): One of the biggest deviations from earlier scales occurs in the Jurassic, at the beginning of the Triassic, with this 190 m.y. for the Palisades and 169 m.y. for the Jurassic. On what was this based?

KULP: That was the report of Curtis.

HURLEY: For what it is worth, my associates and I have measured a K-Ar age on biotite separated from the so-called tin granite from the island of Billiton in Indonesia. This granite has metamorphosed the Triassic fossils in the host rocks, in fact, actually replaced them with tin mineralization. We repeated the age measurements three times and arrived at a value of  $180 \pm 5$  m.y. According to R. W. van Bemmelen,<sup>1</sup> the tin granites were formed after the oldest of the post-Triassic intrusions of diabase. Westervelt<sup>2</sup> prefers to date the Mayalan orogeny as late Jurassic. The sample was sent by H. M. E. Schurmann *et al.*,<sup>3</sup> who have been studying the age of several rocks of considerable geological significance by several methods of age determination. I have no reports of other measurements on this same sample at the present time.

KULP: Faul did not mention his work in the Permian in the Oslo region of Norway. Would he like to say anything about that?

H. FAUL (*United States Geological Survey, Washington, D.C.*): That report has been published for some months.<sup>4</sup> It is 270 m.y. on Pb-U in a zircon and K-Ar in the biotite of a post-Rotliegendes horizon. That is all I can say about it at the moment.

KULP: I understand that the paleobotanist O. A. Hoeg feels that the most probable age for the sequence is the Middle or the Lower Permian, but of course there is a wider possible range in this.

FAUL: I am a fundamentalist when it comes to stratigraphic correlation. I have not seen these field relationships and what differences I have seen are pretty general. Therefore I do not wish to become too involved. I know that it is post-Rotliegendes, but I think one should be aware that these are tentative things.

We are approaching a philosophical subject. I am here probably a member of a small minority. I feel that the establishment of time scales is something that Arthur Holmes was free to do 15 years ago with nothing but A. O. C. Nier's impressive collection of data. Luckily for Holmes, he selected his analyst wisely. With his profound geologic insight Holmes was able to generalize the stratigraphic relationships and come up with a good table. Today, however, we have to be much more careful stratigraphically and analytically. I refer to the many "minimum ages" that occur because we do not know the tops stratigraphically or because there are disturbances of the parent-daughter ratio. I feel that much caution is in order.

KULP: I agree with you on this question. I think that one of the purposes of this monograph is to try to evaluate the parameters you mention.

Another interesting point with regard to Holmes is that his first time scale was published in 1913. Holmes revised it in 1927 and this was not substantially revised after A. O. C. Nier's data. In fact, the scale that our new data suggests now requires only an over-all revision of his original scale of about 20 per cent. With current work we can expect a continuous refinement in the time scale.

I noticed a skepticism concerning the Plevaya K-Ca date. Does anybody have some information that would support or negate this work?

G. J. WASSERBURG (*California Institute of Technology, Pasadena, Calif.*): If you include such data at all you should also include the  $K^{40}$ - $Ca^{40}$  of 100 m.y. determined by Inghram *et al.* on a Permian sylvite. Considering the experi-

mental difficulties and our ignorance of the meaning of results on such soluble salts as sylvite, it would seem better to avoid such unsubstantial data.

KULP: The concordance of the K-Ar and K-Ca dates on the one Plevaya sample is impressive. The analytical work appears to be carefully done. Possibly Inghram *et al.* had a sample that had been recrystallized whereas the Plevaya sample was not. In any event, it seems impossible for the K-Ar age on sylvite to be too high.

R. W. FAIRBRIDGE (*Columbia University, New York, N.Y.*): To the stratigraphers present that date from the Kuttung (of eastern Australia) is very interesting because, if I take it correctly, it is for the volcanics that are associated with the late Carboniferous glaciation. That is a mountain glaciation in New South Wales. It is not the Permian glaciation. The Permian glacial and the Permian marine beds overlie the Kuttung unconformably so that it would appear to be definitely Carboniferous and not Permian.

WASSERBURG: May I ask Lambert if he would care to comment in summary on the difference between the first work published on the times and the materials he presented today.

R. ST. J. LAMBERT (*Oxford University, Oxford, England*): I prefer concerning this matter to say that my colleagues are actually working now on this problem. We had a large number of very systematic figures obtained by the total volume system and, when the new analyses became available, it was quite clear there was a large discrepancy. The discrepancy is different from the Hercynian and the Caledonian dates with the checks we obtained. We have done, I think, altogether five checks ranging in age from 360 to 1600 m.y. In every case, we get a virtually identical argon content. That is to say, within the experimental error.

My colleagues are at the present time building a "Reynolds"-type mass spectrometer and we have one new fusion system; we can verify the old and build others. We have plenty more of the same minerals and we shall be investigating these. We hope to report, possibly by the end of this year, upon this physical problem.

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## Part IV. The Age of the Basement Rocks of the World: North America

### THE NORTHERN APPALACHIANS

P. M. Hurley

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A study of the geological age relationships in the igneous and metamorphic rocks of the northern Appalachians in the United States has been started by a group at Massachusetts Institute of Technology. Work reported to date includes the following data (exclusive of annual reports of the project).

An extensive program of age measurements on the granitic rocks of Nova Scotia, Canada (Fairbairn *et al.*, 1960), using Rb/Sr and K/Ar relationships in micas and feldspar, showed an age range from 300 to 400 million years (m.y.). Samples from 27 localities represented a fairly complete coverage of the main batholithic masses in the province. At two localities, where nearby intrusive contacts with Lower Devonian fossiliferous sedimentary rocks are established, the best estimate of the age of the intrusive rocks is  $365 \pm 20$  m.y. This fact demonstrated that the Lower Devonian was older than 365 m.y. This age also represents a good average figure for the principal activity of the Acadian orogeny elsewhere as well as an average for Nova Scotia.

In the Boisdale Hills on Cape Breton Island, biotite and potassium feldspar in granite, believed to be intruding the nearby Middle Cambrian sedimentary rocks, gave an age of  $500 \pm 20$  m.y. If the intrusive nature of the contact is more solidly disclosed by further field work, this age would provide a much-needed minimum for the Middle Cambrian. In Newfoundland two unpublished Rb-Sr measurements on feldspar by Fairbairn disclosed that both Acadian and Grenville ages would be found in this area. Thus it is apparent that pre-Acadian granitic plutons existed in this extreme eastern belt before the major Acadian orogenic development took place.

In New Brunswick, Tupper (1959) in collaboration with S. R. Hart, found that the granitic batholiths in the Bathurst region gave ages of close to 400 m.y. These are also post-Lower Devonian. This extends the Acadian plutonic activity over a considerable span of time. Similar older ages have been called to our attention by H. Faul (personal communication) who has also been working in the New England area.

In the vicinity of Jackman, in northwestern Maine, a quartz-monzonite stock intrudes well-dated Lower Devonian slate. A collaborative study by several workers (Hurley *et al.*, 1959) on this key locality has shown that the Lower Devonian Oriskany-type fauna antedates the well-measured age of 360 m.y. derived from several samples of intrusive and host rocks. This date is characteristic of the values found in obviously older gneisses in the region as well as in many large plutons showing intrusive relationships with them. Thus it is concluded that the Acadian orogeny was the most recent major episode involving intrusion, metamorphism, and uplift in the greater part of northern Maine, New Brunswick, and Nova Scotia. Unpublished measurements in Vermont suggest that the northern part of this state may also fit into



this category. Also the northeastern coastal region in Maine has shown no values low enough to suggest any significant later activity.

In a study of age values related to well-dated Pennsylvanian sediments in the Narragansett Basin in Rhode Island (Hurley *et al.*, 1960) use was made of granite intrusives and metamorphism to establish a minimum age of 255 m.y. for this period. As this date is essentially the same as that found for the pegmatites of the Middletown area in Connecticut (Nier *et al.*, 1941; Wasserburg *et al.*, 1956) that was used by Holmes (1947) as the time of the Acadian in his well-known time scale, it is of interest to note that these pegmatites now appear to be associated with the event that disturbed the Pennsylvanian section in Rhode Island. These authors therefore have suggested that the terms Acadian and Appalachian be related to events centering about the dates 360 and 260 m.y. respectively, and the term Taconian be reserved for some older date yet to be established with reasonable certainty. In his new time scale, Holmes (1960) has recognized this change.

The White Mountain magma series of New Hampshire mapped by Billings *et al.* (1952) has been dated by several investigators including ourselves, with a well-established figure of 170 to 180 m.y. appearing for the Conway granite at Red Rocks, N.H. This younger and sizeable intrusive therefore postdates the remainder of the Appalachian system and, according to present concepts of the time scale, would fall in the late Triassic or, possibly, even early Jurassic. Somewhat similar alkali intrusive granites in Quincy and Cape Ann, Mass., and Litchfield, Me., do not correspond in age to the Conway granite but are older.

Finally, the belt of unusual alkaline stocks of the Monteregean Hills type, which appears to extend into the northwestern part of the Appalachian system, shows a tentative age of 95 m.y. (Fairbairn, personal communication). This is therefore the youngest igneous activity known in the eastern part of the continent, corresponding to the Upper Cretaceous in current estimates of the time scale.

A considerable number of unpublished measurements on crystalline rocks elsewhere in the northern Appalachians have generally given ages equivalent to the Acadian, the Appalachian, or somewhere between the two. It is known from stratigraphic relationships, however, that there are large areas of older rocks involved in the system, and work is now in progress by several investigators that undoubtedly will disclose this fact by improved geochronological methods. For example, Fairbairn and Pinson (personal communication) have stated that whole-rock  $\text{Sr}^{87}$  ages on the wall rocks of the Middletown, Conn., pegmatites show ages extending into the Pre-Cambrian.

This is not intended to be a comprehensive review of the geochronological work that has been done in the northern Appalachians. Numerous measurements have been made using the lead-alpha method (Lyons *et al.*, 1957; Quinn *et al.*, 1957; Webber *et al.*, 1956). Much of the older work is summarized and compared in an excellent review paper by Rodgers (1952). Also, the work of the Lamont group in the vicinity of New York, N.Y., is covered elsewhere in this monograph. In general, however, the work has indicated generally the same trends as mentioned above. The Appalachian ages are dominant in



eastern Connecticut, Rhode Island, a few local areas in Massachusetts and New Hampshire, and most of southern Maine. Mixed ages between Appalachian and Acadian fill out most of the remainder of the area, particularly in the western parts of New England joining the regions of Acadian ages outlined above.

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# ISOTOPIC AGES FROM NORTHERN NEW JERSEY AND SOUTHEASTERN NEW YORK\*

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The area studied in this investigation encompasses the Manhattan Prong (the city of New York, Westchester County, N.Y., and the adjoining corner of Connecticut), the New Jersey-New York Highlands (Reading Prong), and a metamorphosed Cambro-Ordovician sequence in Dutchess County, N.Y., north of the Highlands (FIGURE 1).

## *Manhattan Prong*

The metamorphic rocks of the Manhattan Prong are composed of three units: the Fordham gneiss (oldest), Inwood marble, and Manhattan schist and gneiss (youngest). Interbedding of lithological types indicates that deposition of these formations was practically continuous. The rocks subsequently have been isoclinally folded and subjected to high-grade metamorphism. The two largest igneous bodies in the Manhattan Prong are the Cortlandt basic intrusion and the Peekskill granite, both of which crosscut the New York City group.

The age of initial deposition has been debated for more than a century and is not yet unambiguously resolved, alternative interpretations being either Pre-Cambrian or Cambro-Ordovician. If deposition occurred during Cambro-Ordovician time, the Prong rocks may or may not correlate in turn with the Cambro-Ordovician rocks in Dutchess County. Unfortunately the Highlands barrier between the Manhattan Prong and the Dutchess County area is complete; thus there is no possibility of correlating the two areas directly by walking out outcrops. A roundabout correlation through Connecticut may be possible but has never been performed.

The potassium-argon ages on mica are summarized in FIGURE 2. Fourteen samples representing the major rock units agree within experimental error at 365 million years (m.y.). In addition, U-Pb ages on pegmatitic uraninite (Wasserburg *et al.*, 1956) and cyrtolite (Nier, 1939) are in good agreement with the K-Ar data. The consistency of these ages strongly indicates that the latest metamorphic or thermal event occurred about 360 m.y. ago. Of seven Rb-Sr ages, five are in essential agreement with the K-Ar ages on the same mica and two ages fall somewhat low.

Along the western border several higher K-Ar ages are found (the maximum being 475 m.y.), indicating that the Prong had been metamorphosed prior to 360 m.y. ago. The ages in the low 400 m.y. range are interpreted as due to partial loss of argon from older mica during the 360 m.y. event. Age results from Dutchess County (discussed later) clarify the problem of whether the highest Manhattan Prong age of approximately 470 m.y. corresponds to the true time of the earlier event or is merely the result of the 360 m.y. reheating on an even older original age.

\* Lamont Geological Observatory Contribution No. 462.

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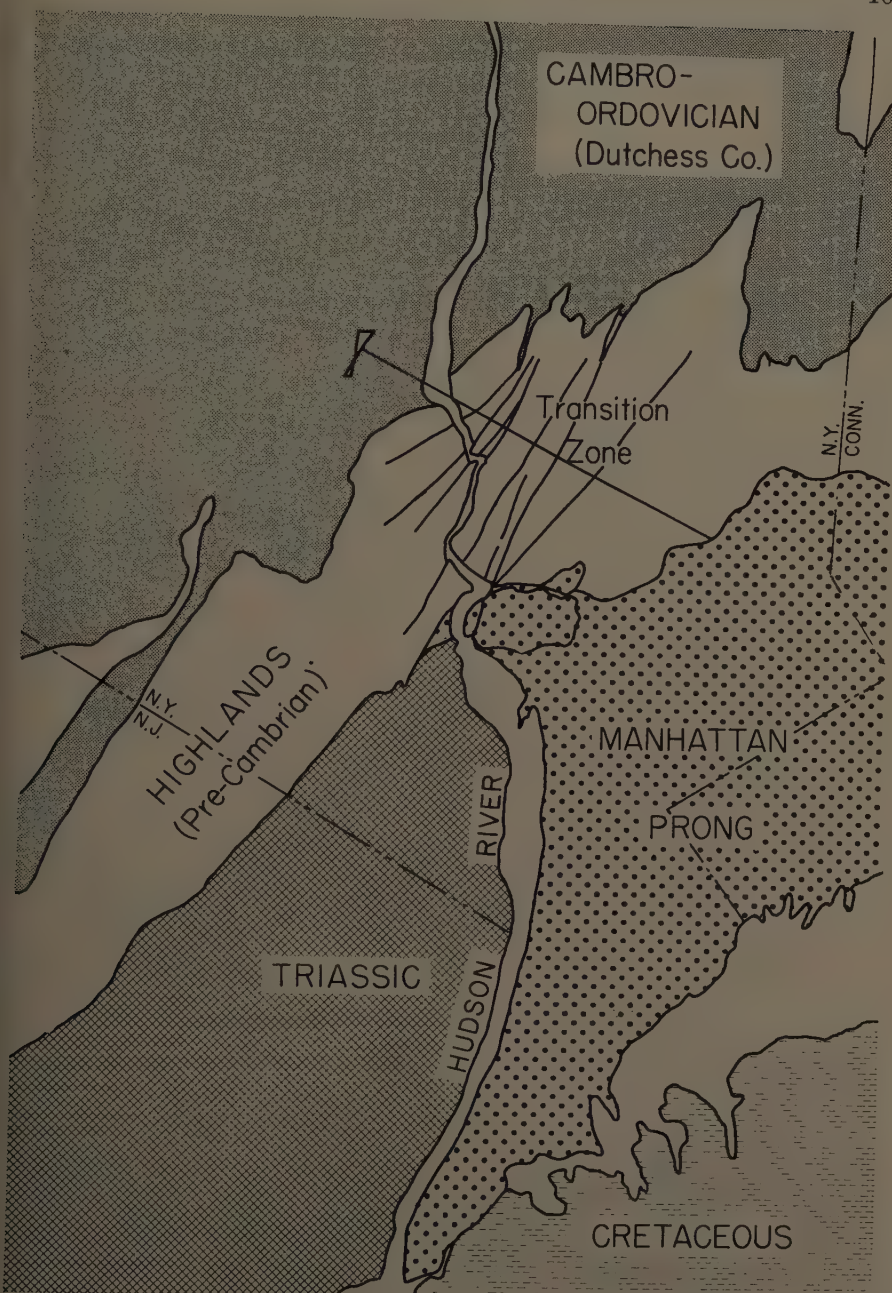


FIGURE 1. Generalized geology of northern New Jersey and southeastern New York.

The K-Ar age of 435 m.y. from the Cortlandt Complex suggests that it may have been emplaced during the original metamorphic cycle. Since the complex is practically undeformed, it is suggested that the 360 m.y. event consisted of a mild pervasive reheating, possibly accompanied by intrusion of numerous

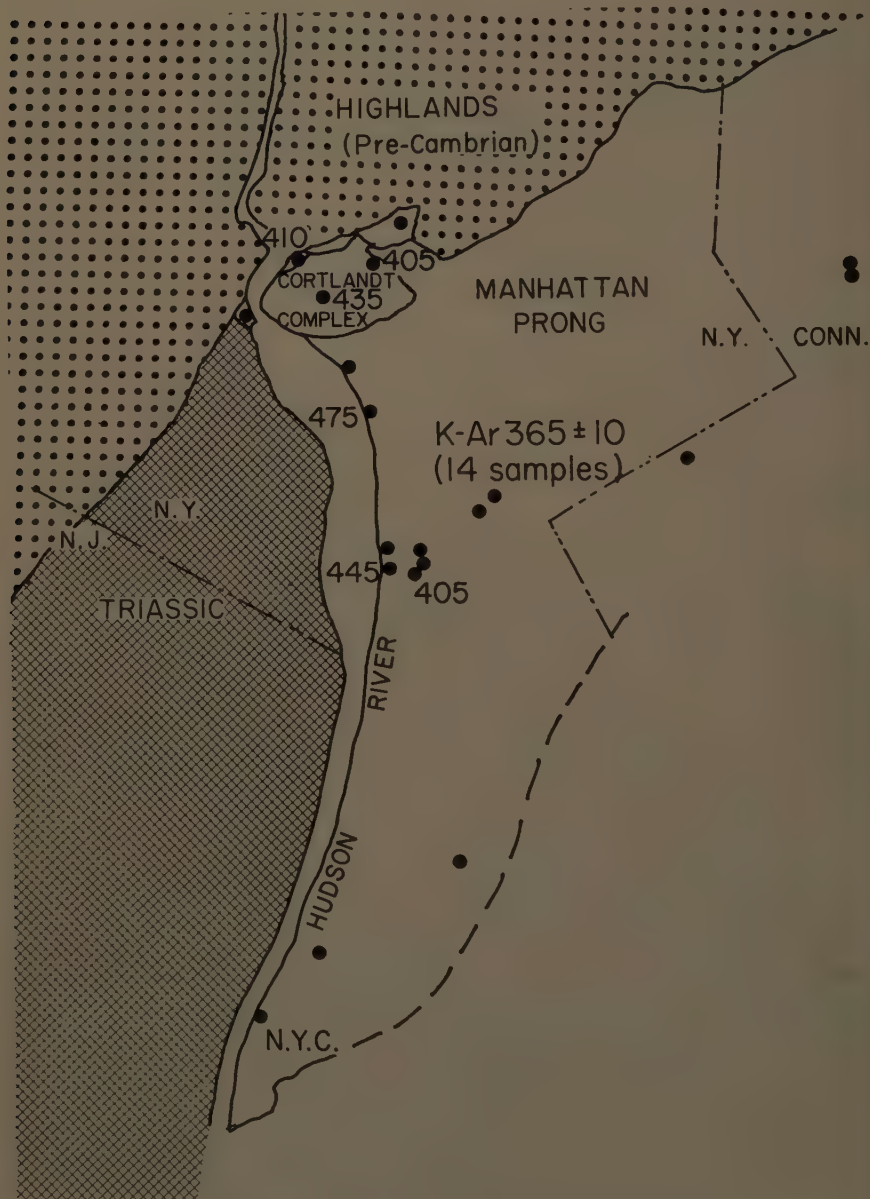


FIGURE 2. Potassium-argon ages on mica from the Manhattan Prong.



pegmatites, but did not involve intense deformation. In the central and eastern portions of the Prong no ages higher than 360 m.y. are preserved. In the western margin, significantly higher ages (400 m.y. and older) are interspersed with ages of approximately 360 m.y. indicating that the younger event did not completely overlap the older event to the west but nevertheless was strongly felt in restricted local areas.

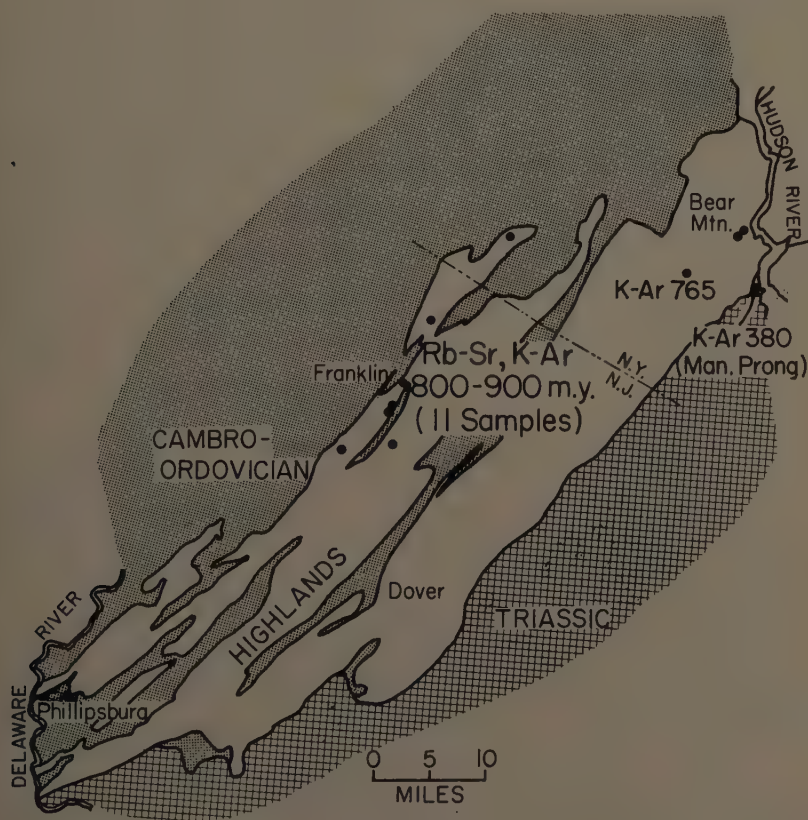


FIGURE 3. Mica ages from Reading Prong.

### *Reading Prong*

The Reading Prong ("Highlands" in FIGURE 1) is a crystalline belt of known Pre-Cambrian age extending from Reading, Pa., through western New Jersey and southeastern New York into western Connecticut. Eleven K-Ar and Rb-Sr mica ages from the Highlands at least 10 miles from the zone affected by the Paleozoic events agree within experimental error at approximately 830 m.y. (FIGURE 3). U/Pb ratios in two zircon samples from Bear Mountain, N.Y. (Tilton *et al.*, 1958) suggest an original age of 1100 to 1150 m.y. for that part of the Highlands. If this be true, the mica ages could be attributed to a subsequent distinct thermal or metamorphic event at approximately 830 m.y.



or they could represent the effect of the Paleozoic metamorphism(s) on mica having an original age of 1100 m.y. The first interpretation is favored, inasmuch as 800 to 900 m.y. ages are encountered over wide areas and at distances of 30 to 40 miles west of the nearest exposed rocks of the Manhattan Prong. It is not until the Highlands trend directly into the zone metamorphosed during the Paleozoic, east of the Hudson River, that the ages of the old mica are markedly altered.

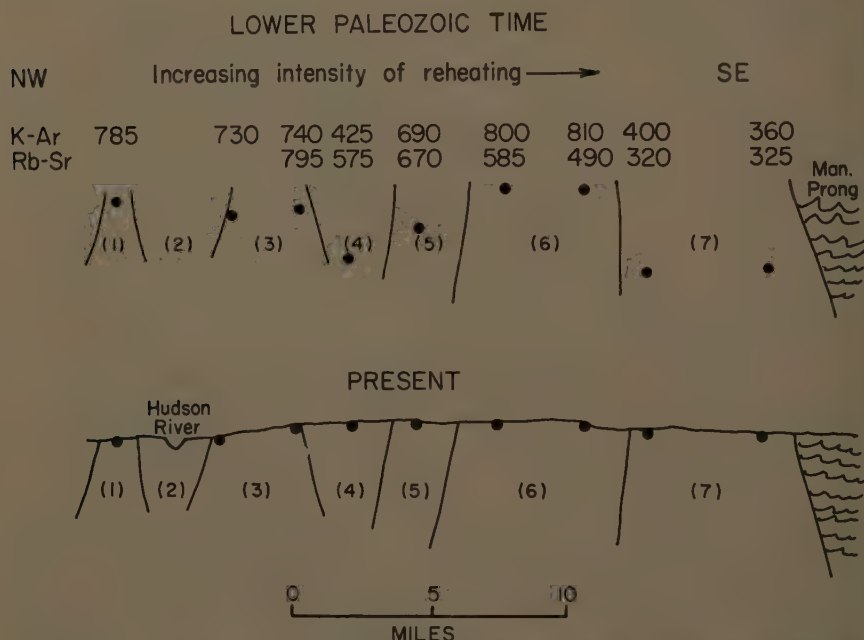


FIGURE 4. Cross section through the Highlands transition zone indicating isotopic ages and inferred structure.

### *Highlands Transition Zone*

In this area (FIGURE 1) the old Highlands rock has been extensively remetamorphosed during Paleozoic time. A northwest to southeast profile of samples was collected along the line indicated in FIGURE 1, from an outlying fault block west of the Hudson River to an eastern terminus approximately at the longitude of the central Manhattan Prong. Berkey and Rice (1919) mapped a number of crossfaults cutting this portion of the Highlands.

In FIGURE 4, mica ages obtained in the traverse are shown together with an interpretation of their pattern. It is seen that, in broad aspect, the apparent ages decrease from virtually unaffected, typical Highlands values in the northwest to a sample at the eastern end that has been so thoroughly recrystallized as to lose all of its previously accumulated argon at 360 m.y. In detail, however, the age pattern is highly irregular. The irregularities are considered to be related to the configuration of the fault blocks at the time of the Paleozoic events. For example, the K-Ar and Rb-Sr ages from fault block (4) are lower

than the respective isotopic ages on either side, suggesting that this block was relatively depressed during the Paleozoic and thus suffered more extensive loss of daughter isotopes. By similar reasoning fault block (6) was relatively elevated, a deduction independently supported by geologic considerations (Long and Kulp, in press). The lower portion of FIGURE 4 shows that today all the samples are exposed on the surface.

An additional complication is the observed age pattern whereby the K-Ar age greatly exceeds the Rb-Sr age from the same mica (for example, on fault

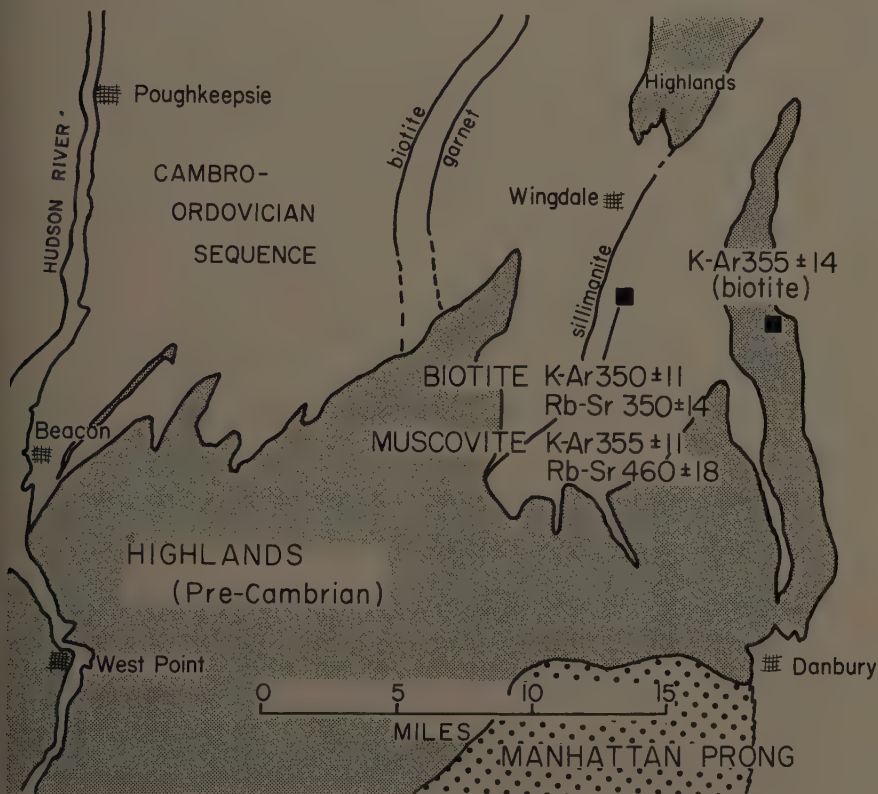


FIGURE 5. Mica ages from the Dutchess County area.

blocks 6 and 7). The same results have been obtained by other workers in similar areas known to have experienced complex metamorphic histories. The mechanism responsible for this is as yet not well understood.

#### *Dutchess County*

In the Dutchess County area, described in a classic paper by Balk (1936), a Cambro-Ordovician sedimentary sequence of quartzite, limestone, and pelite is progressively metamorphosed from west to east. North to south-trending biotite, garnet, and sillimanite isograds may be traced. A sample of Hudson River pelite from the sillimanite zone gave mica ages seen in FIGURE 5. The

biotite K-Ar and Rb-Sr ages and muscovite K-Ar age are in excellent agreement with the 360 m.y. ages in the Manhattan Prong. The Rb-Sr age of  $460 \pm 20$  m.y. on muscovite seems to point to a prior metamorphic event. Since, according to some of the latest revisions of the geological time scale, the mid-Ordovician Hudson River pelite could not have been deposited much prior to this time, the determined age of 460 m.y. must be the true age of the initial metamorphism within narrow limits. In this case the highest age of about 470 m.y. found in the Manhattan Prong is very likely the true age of the same event.

In conclusion, a thorough search in the Manhattan Prong has revealed no evidence for a metamorphic episode older than a known lower-Paleozoic event. Geological relationships, while inconclusive, are mildly weighted in favor of a Cambro-Ordovician age of deposition for the Prong rocks, a hypothesis not in disagreement with existing isotopic data.

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### Discussion of the Paper

G. J. WASSERBURG (*California Institute of Technology, Pasadena, Calif.*):

In collaboration with Engel of California Institute of Technology we have done some work on the Edwards-Balmat district of New York. This lies in the Grenville Province. We obtained the following ages:

Phlogopite GMW-1-A	960 m.y.
Phlogopite GMW-1-B	1170 m.y.
(from marble in Balducci Quarry, Gouverneur, N.Y.)	
Muscovite	980 m.y.
(collected by Buddington)	

Pegmatite (Whippoorwill Corners, N.Y.)

There is a spread of 20 per cent in the values. This is well outside of experimental error. The phlogopite samples are from the same hand specimen. "A" is the coarse-grained fraction.

These values lie in the time band characteristic of the so-called Grenville metamorphism. The older age records a rather high value close to the Pb-U ages obtained by Tilton on zircons from the Storm King granite.

L. O. NICOLAYSEN (*Bernard Price Institute of Geophysical Research, Johannesburg, Union of South Africa*): Could Long give us an idea of the proportion of radiogenic strontium to total strontium in his samples and whether there was any indication of variation in this ratio going from east to west through the Highlands transition zone?

LONG: These samples were all biotite. The ratio of radiogenic  $\text{Sr}^{87}$  to total  $\text{Sr}^{87}$  varied from about 0.3 to 0.8, with no apparent correlation with either the age or the position of the sample in the profile. The lowest concentration of common strontium was about 0.4 ppm and the highest about 25 ppm.

NICOLAYSEN: Do you not think, with the Rb-Sr date of 460 m.y. that you reported from Dutchess County, that the problem of correction for the non-radiogenic component might be important?

LONG: Yes. If you bring the 460 m.y. age down to 350 m.y. by changing the composition of the common strontium, a 6 per cent change in the  $\text{Sr}^{87}/\text{Sr}^{86}$  is necessitated for this mica. This would bring the strontium age on the biotite down to about 340 m.y. (the change in common strontium composition would have relatively little effect on the biotite because it was practically strontium-free). Six per cent sounds like a large number. An analysis of the strontium isotopic composition of the whole rock is being done to check this point.

R. D. RUSSELL (*University of British Columbia, Vancouver, B.C., Canada*): Can you give the value of the rubidium decay constant used in this calculation?

LONG: I used the new value determined by Flynn and Glendenin that is,  $\lambda_{\text{Rb}} = 1.47 \times 10^{-11} \text{ yr.}^{-1}$ .

# POTASSIUM-ARGON ISOTOPIC AGES ON MICAS FROM THE SOUTHERN APPALACHIANS\*

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## *Introduction*

Previous work (Long *et al.*, 1959; Tilton *et al.*, 1959) has shown that the basement of the western part and, possibly, the whole of the southern Appalachians, was formed at least 850 million years (m.y.) ago. The  $\text{Pb}^{207}/\text{Pb}^{206}$  dates on zircon (Tilton *et al.*, 1959) show that crystalline rocks existed in the area at least 1250 m.y. ago. The zircon from Shenandoah National Park in Virginia that yielded concordant U-Pb ages suggests consolidation of igneous rock in that area at about 1100 m.y. ago. Although some evidence exists (Long *et al.*, 1959) for a metamorphic event between 850 m.y. and 350 m.y. ago in the southern Appalachians, it appears to have been largely obliterated due to the superimposition of the 350 m.y. activity. The existing ages on micas show that the metamorphic action at about 350 m.y. has been observed throughout the length of the Appalachians. The earlier data of the Lamont group also showed the presence of a younger metamorphic event in the southeastern Piedmont.

The data presented here are part of a continuing study of the metamorphic-plutonic history of the Blue Ridge and Piedmont Provinces. A comprehensive suite of metamorphic and igneous rock samples was collected in the summer of 1959 with the aid of numerous geologists familiar with the detailed local and regional geology. The purpose was to extend the knowledge obtained by the previous study and to attempt to answer certain remaining questions. The initial part of the study constitutes K-Ar isotopic age measurements on micas from these rocks. This will be followed by measurements by other isotopic methods on appropriate minerals as these are warranted. The high sensitivity of mica, particularly fine-grained biotite, to loss of radiogenic argon because of temperature rises makes this mineral most useful for defining the last thermal event that a given rock has experienced.

The samples which have been analyzed are reported in TABLE 1 and are located in FIGURE 1. The isotopic ages in the figures are given only to the nearest five million years. The analyses for potassium and radiogenic argon have been made by standard isotope dilution techniques employed in this laboratory (Long and Kulp, in press). The accuracy of the isotopic ratios from which the isotopic ages are calculated is about 3 per cent, so that the analytical error on the calculated ages in this age range is only about  $\pm 10$  m.y. The interpretation of these results includes consideration of previously published isotopic data and takes into account relevant field and petrographic observations.

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*Blue Ridge Province*

The K-Ar mica ages obtained on samples from the Blue Ridge Province of western North Carolina are shown in FIGURE 2. The broad picture is that

TABLE 1  
POTASSIUM-ARGON MEASUREMENTS ON MICAS IN THE PIEDMONT AND BLUE  
RIDGE PROVINCES

Sample No. and mineral*	Location	Rock unit	%K	Radiogenic Ar scc./gm. $\times 10^8$	Isotopic age (million years)†
Blue Ridge of western North Carolina					
K-78 M	Waynesville	Carolina gneiss	6.85	10.27	344
K-84 B	4 miles west of Soco Gap	Carolina gneiss	7.15	11.24	359
K-86 B	5.6 miles southeast of New-found Gap	Ocoee series	6.40	10.78	382
Blue Ridge of southwestern North Carolina					
K-11 B	Andrews	Valleytown fm.	6.76	11.07	373
K-12 M	Ducktown	Ocoee series	6.85	9.73	327
K-16 B	Ducktown	Schist inclusion in ore	8.41	13.83	374
				13.51	366
K-23 B	Franklin	Carolina gneiss	6.72	8.90	307
Georgia Piedmont					
K-24 B	Atlanta	Granitic gneiss	7.91	10.65	311
K-30 B	Tyrone	Porphyritic granite	8.02	9.85	286
K-32 B	Lorane	Migmatite	8.53	9.24	254
K-35 B	Sparta	Granite	6.21	8.01	299
K-36 B	Greensboro	Palmetto-type granite	7.11	7.92	261
K-37 B	Athens	Migmatite	7.08	7.95	263
South Carolina Piedmont					
K-61 M	Inmo	Phyllite, Carolina slate belt	7.84	9.97	296
K-72 B	Easley	Granitic gneiss	7.48	9.29	289
North Carolina Piedmont					
K-101 B	Nello Teer Quarry, Wake County	Granite	7.49	7.55	238
K-106 B	Graystone Quarry, Henderson	Migmatite	5.89	6.51	259

\* B = Biotite, M = Muscovite

†  $\lambda_{\beta} = 4.72 \times 10^{-10} \text{ yr.}^{-1}$ .

$\lambda_{\alpha} = 0.584 \times 10^{-10} \text{ yr.}^{-1}$ .

of an ancient basement that has been reheated about 350 m.y. ago, as previously discussed in some detail by Long *et al.* (1959). In the profile from the north end of the Spruce Pine District to Pardee Point the K-Ar ages on the same rock unit rise regularly from the value of about 350 m.y. (the mica age of the Spruce Pine pegmatites) to 800 m.y. at Pardee Point (L-146, 355 m.y.; L-22,

420 m.y.; L-333, 525 m.y.; L-332, 640 m.y.; L-331, 650 m.y.; and L-149, 800 m.y.). Southwest along strike the same pattern is repeated in micas of various rock types, for example, L-141, 355 m.y.; L-330, 695 m.y.; K-78, 345 m.y.; K-84, 360 m.y.; and K-86, 380 m.y.

The sample K-23 that gives an isotopic age of 307 m.y. was probably affected by the younger thermal event in the Piedmont that is discussed below.

In the area between Waynesville and Bryson City field studies by Hadley *et al.* (1955) have established the existence of two stratigraphic units each

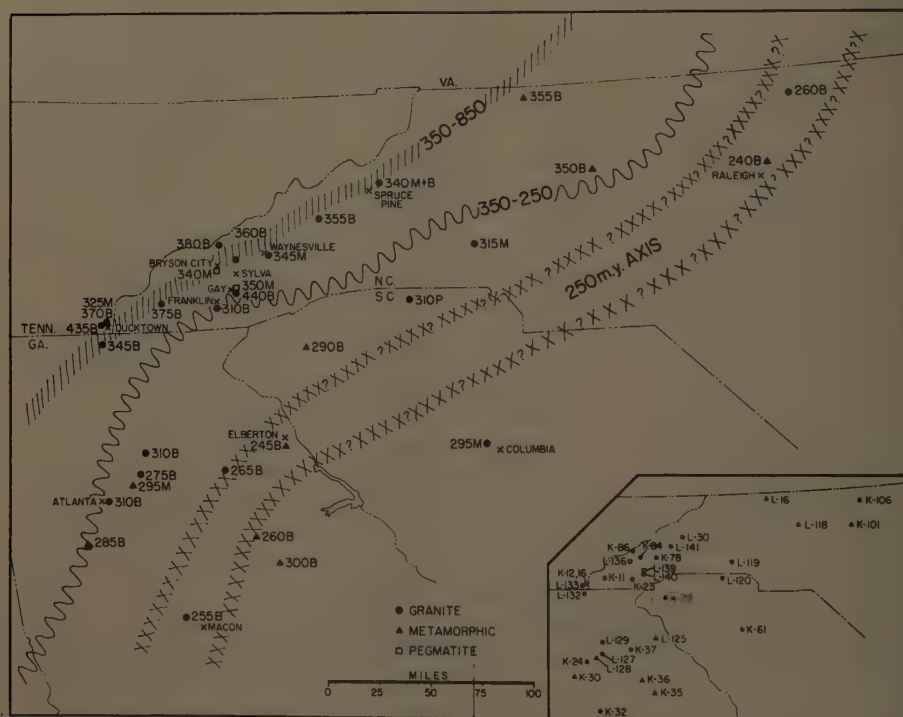


FIGURE 1. K-Ar isotopic age measurements and apparent boundaries of thermal effects on the micas, southeast United States.

with its own structural and metamorphic history (FIGURE 2). The older consists of strongly deformed basement schists and gneisses clearly resembling rocks at Spruce Pine. The metamorphic grade in this unit increases from southeast to northwest. The younger unit (Ocoee series) rests unconformably on these basement metamorphic rocks and was in turn subsequently deformed and metamorphosed, with the grade increasing from west to east. Thus a period of erosion, deposition, and metamorphism followed the formation of the basement crystallines.

In this area, Ocoee rocks pinch out to the southeast between Bryson City, to the west and Waynesville, Sylva, Gay, and Franklin to the east. Since



the thermal gradient of the post-Ocoee metamorphism was opposite in direction to that observed in basement rocks, the basement rocks were retrograded in the northwest while already formed gneisses to the southeast were remetamorphosed under conditions locally approaching granitization. New data available here are presently restricted to the basement and include samples K-78 and K-84 with isotopic ages on biotite of 345 m.y. and 360 m.y., respectively. These values are within the experimental error of 350 m.y. that appears to have been the time of formation of the pegmatites in the Bryson City (L-136) and Franklin-Sylva districts (L-139). Sample K-84 is from an area where deformation and erosion have combined to expose the underlying basement northwest of the margin of the Ocoee series (FIGURE 2). These new dates serve to extend the 350 m.y. Spruce Pine metamorphism considerably southwest of the Spruce Pine-Stockville area. This was not completely unexpected in view of earlier results reported by Long *et al.* (1959), to the southwest. Although the pegmatites at Bryson City and Gay were formed at about 350 m.y., the Carolina gneiss host rock at Gay (L-140) gave an apparent K-Ar age of 440 m.y. for biotite. Since the K-Ar age for the host rock is minimal, the emplacement of the pegmatites at Gay, identical in time and mineralogy to those at Spruce Pine, was not accompanied by complete reconstitution of the host rocks. This is consistent with the observation of J. C. Olson (1946) that these pegmatites were intruded into joints that transect the structure while at Spruce Pine they are almost all conformable and intruded into plastic country rock.

At present it would seem that the 350-m.y. metamorphic episode in this area was also superimposed on the already metamorphosed Ocoee rocks and that the earlier plutonic history, seen from field studies of basement rocks, has been largely obliterated as far as K-Ar ages are concerned.

#### *The Ducktown Area*

The metamorphic history of Ocoee sediments has also been investigated to the southwest at Ducktown. The structural and metamorphic evolution of the Ocoee series here has been worked out by Hurst (1955) and includes two distinct periods of deformation with recrystallization of the rocks completed at the end of the first period of folding (page 99). Emplacement of sulfide ore at the Ducktown mine postdates the last deformation. Subsequent to these events, pervasive alteration of all rocks in the Mineral Bluff quadrangle southwest of Ducktown resulted in chloritization of biotite, hornblende, and garnet, clouding of feldspars, and redistribution of sulfides in the rock. Similar effects are seen in the Ducktown area where coarse staurolite crystals have been replaced in part and in whole by sericite (O. Kingman, personal communication).

Sample L-132 from McCaysville, Ga., gives an average age of about 335 m.y. The rock consists of fine-grained muscovite and biotite from a highly altered shear zone in the Copperhill formation. The mica formed during shearing may be older than the 350 m.y. event but lost its accumulated argon due to the thermal rise at 350 m.y. and/or 250 m.y. Other measurements in this area give evidence for argon loss or crystallization at these times, that is, K-12, 325 m.y. and K-16, 370 m.y. Sample K-12, collected underground in

the Ducktown mine, is part of the Ocoee series and was obtained 250 feet across strike (approximately northwest) from the footwall of the ore body. Staurolite in the area has been extensively altered to sericite, and hence the date is interpreted as most likely reflecting the final retrograde metamorphism identified by Hurst (1955) in the Ocoee series of the Mineral Bluff Quadrangle of northwest Georgia.

Sample K-16 is a dense biotite schist from an inclusion in the heart of the sulfide ore body. The average of two K-Ar determinations gives an age of 370 m.y. with a standard error of less than 5 m.y. This is analytically older than 350 m.y. and might suggest that the Ducktown ore was emplaced prior to 350 m.y. ago. If the biotite was not produced by the ore, the ore may be younger than 350 m.y.

Sufficient data have now accumulated to make it reasonably certain that a metamorphic event occurred in this region between 350 and 850 m.y. ago. All of the existing data can be fitted into an interpretation that calls for a metamorphic event in the middle Ordovician at about 450 to 470 m.y. ago. Such an event has been established in Dutchess County, N.Y., by L. E. Long (private communication). The evidence for a metamorphism between 850 and 350 m.y. in the southern Appalachians may be summarized as follows:

1. The late Pre-Cambrian Ocoee sediments that were deposited on the basement metamorphic complex were metamorphosed prior to the 350 m.y. event (L-133). Sample L-133 is fine-grained biotite from a graywacke of low metamorphic rank.

2. The dikes at Red Hill sharply crosscut, brecciated, previously metamorphosed basement rock but were themselves subsequently metamorphosed (Kulp and Poldervaart, 1956). The K-Ar ages of 435 and 455 m.y. show that this metamorphism occurred earlier than the 350 m.y. metamorphism.

3. Mica in the metamorphosed sediments of Cambrian age (K-11) gives a K-Ar age of 373 m.y. that is analytically older than the 350 m.y. event, yet the sedimentary rock from which this fine-grained granoblastic quartz-biotite-muscovite schist was derived was almost surely formed less than 600 m.y. ago.

The combination of data indicates that the intermediate metamorphic event occurred subsequent to formation of Cambrian (lower?) sediments but pre-455 m.y.; hence a probable age for this event of 450 to 550 m.y. appears most reasonable.

### *Piedmont Province*

Isotopic ages for the Piedmont Province are, as yet, fewer in quantity and spread out over a much larger area of probably equal geologic complexity to that of the Blue Ridge in Virginia. The absence of any ages older than the Paleozoic is an important feature. Nevertheless, the pattern of multiple metamorphism in a single large area is present. The youngest reliable ages (K-32B, 255 m.y.; K-101B, 240 m.y.; K-106B, 260 m.y.; and L-125B, 245 m.y.) average about 250 m.y., identical to the values obtained for the pegmatites near Middletown, Conn., in the New England metamorphic-plutonic province. (The sample L-124, reported by Long *et al.* [1959] from Cayce, S.C., which gave a K-Ar age of 230 m.y., is omitted since it is at least half chlorite and prob-



ably has not retained all of its argon.) One of these young ages is obtained from Neuse, N.C., the others from south and central Georgia.

The regional picture for the Georgia Piedmont as developed by V. Hurst (private communication) consists of an axis of intense metamorphism, migmatization, and granite emplacement located approximately along a line between sample K-32 northwest of Macon and sample K-37 from Athens. Most events to either side appear to be older and variously affected by this superimposed younger event. Petrographic and age data at present seem consistent with this broad generalization. Sample K-32 northwest of Macon and sample K-37 from Athens have K-Ar ages of 277 m.y. and 265 m.y., respectively. Both samples are of biotite gneiss from which very clean, brown, medium-grained mica was obtained. Chlorite was almost totally absent from both rocks. Long *et al.* (1959) has reported a K-Ar age of 245 m.y. for the biotite from the Elberton granite. The Massachusetts Institute of Technology, Cambridge, Mass., group (Pinson *et al.*, 1957) has obtained Rb-Sr ages on muscovite and biotite from the Elberton, Stone Mountain, Lithonia, and Carolina formations agreeing with these K-Ar results within the analytical errors.

The effects of this 250 m.y. event on the Elberton granite have been studied by Gruenfelder and Silver (1958). They have reported nearly concordant U-Pb isotopic ages on zircons separated from the granite, suggesting crystallization at 450 m.y. or earlier (possibly synchronous with the event that produced the effects described above in the rocks of the Blue Ridge Province). The biotite present is olive green and almost completely free of chlorite. The texture, however, is distinctly metamorphic as first noted by Gruenfelder and Silver (1958). Hence, the picture here is one of magmatic crystallization followed by recrystallization at a much later time. The earlier age is indicated by zircon data, the latter by determinations using mica. A very similar situation appears to exist for sample K-35 from intrusive granite at Sparta. Relic textural features and extensive zoning of feldspar crystals are seen and indicate an igneous origin, while irregular interlocking grain boundaries, alteration of feldspars, and shredding and chloritization of biotite suggest later deformation, alteration, and limited recrystallization. The isotopic age of 300 m.y. probably reflects only partial argon loss due to the reheating from the superimposed event centered to the west and occurring around 250 m.y. ago.

Isotopic and petrographic data for localities west of the Athens-Macon axis seem to point to a similar compound history for the rocks studied. K-Ar data available for the indicated samples (FIGURE 1) range between 275 m.y. and 310 m.y. with rather clear petrographic evidence for a compound history being observed in samples K-30 and K-24 from Tyrone and Atlanta.

Taking into account all of the mica ages (FIGURE 1), it is seen that a 250 m.y. thermal event superimposed on the plutonic-metamorphic province of the Piedmont clearly appears in Georgia and North Carolina. It is bounded on both east and west by rocks only partially affected by the 250 m.y. event. It is possible that instead of the 250 event being represented by two foci in North Carolina and Georgia, it is continuous as suggested in FIGURE 1. This question will be resolved by measurements on additional samples from South Carolina and the southern part of North Carolina. Within the boundaries all of the

rocks were sufficiently heated during the 250 m.y. metamorphism to have suffered complete loss of the accumulated radiogenic argon in their micas. To the northwest a boundary is also inferred, bounding (on the southeast) the area of an ancient basement that had been affected by the 350 m.y. metamorphism but not that of 250 m.y. Further northwest is the boundary between basement rock whose micas lost all accumulated argon at the 350 m.y. event and those only partially affected.

Thus there emerges a whole series of metamorphic episodes that affected the basement rocks of the southern Appalachians. These belts of metamorphism appear to have had roughly parallel axes striking northeast. It also appears that they may have been of decreasing width such that the 850 to 1100 year basement covered the entire area. The 450 to 550 m.y. event did not extend as far west but along its axis produced many of the major granite bodies of the Piedmont such as at the Elberton. The axis of the 350 m.y. event may have been similar in location or may have been farther west as suggested by the line of pegmatites it produced in western North Carolina. Finally, the 250 m.y. event represented only a narrow band of about 20 miles over which the micas were completely outgassed, although second order effects extended for 60 miles to either side of the axis.

Further petrologic and isotopic studies may make it possible to determine the time of initial formation of each of the homogeneous granite bodies of the Piedmont. Such information would be most definitive for determining the location of the axes of these metamorphic epochs.

### *Conclusions*

The rocks of the Blue Ridge Province have been subjected to repeated metamorphic activity. The initial metamorphism of the basement occurred at least 1100 m.y. ago.

A widespread metamorphism may have affected the area at about 850 m.y. ago.

The next clearly defined event took place between about 450 and 550 m.y. ago.

At 350 m.y. ago metamorphism occurred all along the western border of the southern Appalachian province. This may have covered the entire Piedmont also but at present appears to have occurred in a zone at least 100 miles in width. Pegmatites were intruded along the western part of the plutonic-metamorphic province and granite masses were emplaced in the Piedmont.

At a still younger time, about 250 m.y. ago, a belt of metamorphism developed in Georgia that may possibly prove continuous through the eastern Piedmont of South Carolina and North Carolina.

There is some evidence that these four or five successive metamorphic events may have had similar strike but had decreasing widths.

### *Acknowledgments*

We were greatly aided in the sample-collecting phase of the investigation by numerous geologists engaged in studies of local and regional geology in the southern Appalachian metamorphic-plutonic belt. Familiarization with the

detailed geologic setting of samples and results of current field studies in sampled areas was thus made possible and assured the collection of geologically significant samples. The generous cooperation of the following individuals is gladly acknowledged: J. M. Parker, III, North Carolina State College of Agriculture and Engineering, Raleigh, N.C.; Owen Kingman, Tennessee Copper Co.; R. L. Wilson, University of Chattanooga, Chattanooga, Tenn.; H. S. Johnson, South Carolina State Development Board; and J. F. McCauley, University of South Carolina, Columbia, S.C.; V. J. Hurst, Department of Mines, Mining, and Geology, Georgia; and E. L. Hastings, Geological Survey of Alabama. We are further indebted to these workers for many stimulating hours of discussion, continual correspondence throughout the study, and in some instances for pointing out geologically important problems amenable to solution by isotopic age study.

R. Kologrivov, assisted by J. Clark and R. McPherson were largely responsible for the analytical work. The typing and drafting were done by M. Rippey and J. Brokaw.

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### Discussion of the Paper

G. W. WETHERILL (*Carnegie Institution of Washington, Washington, D.C.*): What leads you to interpret the situation of a potassium-argon age of 435 million years (m.y.) and a Rb-Sr age of 330 m.y.? I believe the figures were, as they indicated anything in particular at all with regard to the time of metamorphism, much less than the conclusion that you made.

My associates and I found this situation in different places in the Appalachians and the MIT people have found it, as well as our laboratory, in the Sudbury area. To be sure there are no cases where the K-Ar age is apparently higher than the presumed true age of the rock; in most cases the true age has to be a presumption because of the complexity of the age data. However, I think it is rather premature to say that because we get a K-Ar age of 435 m.y. on this

rock that the rock is certainly older than 435 million years. I do not think this can be interpreted as a minimum age.

KULP: I do not believe there is evidence, either theoretical or observational, that the K-Ar age in micas can be too high. All of the data show micas to be very sensitive to argon loss on slight increases in temperature. There is no evidence that the K-Ar age is ever higher than the last thermal event. I therefore consider the K-Ar age to be a reliable minimum age.

WETHERILL: I do not see how that follows at all. There are a number of measurements now of metamorphic rocks where the K-Ar age is very decidedly higher than the Rb-Sr age on the same mineral. Now, there are several interpretations that can be made of this, some of which imply that it is a minimum age and others that imply that it is not.

One that implies that it is not could be that it represents inherited radiogenic argon from the whole surrounding area at the time of metamorphism. Until this possibility is excluded, I do not think there is any justification in interpreting this as a minimum age.

KULP: In the first place, the fact that the K-Ar age is occasionally higher than the Rb-Sr age on the same mica is no evidence that the K-Ar age exceeds the actual age. In those cases where concordant U-Pb isotopic ages are available, the K-Ar ages are always equal to or less than this age. Second, as reported in an earlier session, extensive base exchange of mica removes argon and potassium either equally or slightly more argon than potassium so that even under this type of drastic alteration the K-Ar age is still a reliable minimum. Third, at Lamont, P. E. Damon has shown the absence of excess argon in other mica structures that do not contain potassium; and Carr has shown that, even at a partial pressure of one atmosphere, negligible argon is taken up by a silicate melt. Finally, the low Rb-Sr ages always occur in biotite not muscovite, and the K-Ar ages agree in these cases on both micas if the same rock is used.

In some cases where muscovite and biotite give the same K-Ar age, a rubidium-strontium age can be obtained that will also agree on the muscovite but may be low in the biotite. This suggests to me that the Rb-Sr age is being altered by preferential removal of radiogenic strontium by base exchange with the ground water.

G. J. WASSERBURG (*California Institute of Technology, Pasadena, Calif.*): To what extent can one say that the micas in the Ocoee series are not detrital micas derived from an older terrain and that this is not simply a partial memory effect?

ECKELMANN: It is generally possible to distinguish detrital mica from that that is completely metamorphic. In the case of the Ocoee rock that we worked on—I presume you are talking about the one west of Ducktown—the complete texture of the rock is metamorphic. It has a schistose fabric that would not be found in metamorphosed sediments in which the micas are sedimentary relics. If the rock is completely recrystallized to get a metamorphic fabric of this kind, it appears impossible for any argon to be retained. Particularly since only light heating, far short of visible recrystallization or alteration, suffices to remove accumulated argon as both S. R. Hart and B. J. Giletti have shown.

L. T. ALDRICH (*Carnegie Institution of Washington, Washington, D.C.*):



One evidence for an event older than 350 m.y. in the Southern Appalachians is in the Spruce Pine pegmatites. The uraninite that I did under the guidance of G. R. Tilton in the Chestnut Flat mine had a  $\text{Pb}^{207}\text{-Pb}^{206}$  age of about 420 m.y. To be sure the two uranium lead ages were concordant, but it was a very radiogenic lead, and it seems to me that there is some evidence down there in the pegmatites themselves for something somewhat older.

KULP: The high sensitivity of the  $\text{Pb}^{207}\text{-Pb}^{206}$  age to the  $\text{Pb}^{207}/\text{Pb}^{206}$  ratio in this age range and the common preferential removal of  $\text{Pb}^{206}$  from uraninite and pitchblende make such evidence questionable. The concordance of the K-Ar ages on micas and Rb-Sr on potash feldspar and the  $\text{U}^{238}\text{-Pb}^{206}$  and  $\text{U}^{235}\text{-Pb}^{207}$  ages on uraninite in the Spruce Pine pegmatites make their formation about 350 m.y. ago highly probable.

K. K. TUREKIAN (*Yale University, New Haven, Conn.*): Can we couple these metamorphic events with the stratigraphic and depositional events in the Appalachians? In the north we have Ordovician and Devonian deltas to which the 450 and 350 m.y. events might be coupled. I recall that in the south similar Ordovician stratigraphic events are recorded but not Devonian. Is this correct, Kay?

M. KAY (*Columbia University, New York, N.Y.*): All this is quite true. For example, if you go to western Georgia or in eastern Tennessee where the Paleozoics are preserved, you have things like the Chattanooga shale lying directly either on a very thin lower Devonian quartz sand or lying down on Ordovician limestones. There is no suggestion there of Highlands because there should be some large detrital deposit area off to the west.

It is very puzzling from the standpoint of the stratigrapher if, on the one hand we attribute the sediments that are so very thick and so very coarse in West Virginia northward to the Acadian orogeny, then come to the southern area and say that there is the same age metamorphism and intrusions in the southern Piedmont; we lack the very kind of evidence that we originally had to build up the orogeny in the north. Bear in mind that the Acadian orogeny was originally based upon just such things as the stratigraphic record.

I do not know what the explanation is but, on the other hand, if there is metamorphism of that age, there simply is. It is the thing that I used to hear spoken of as "Ayer's Law," anything that did happen can happen.

KULP: This may be evidence that the orogenic events identified from the structure and stratigraphy of sedimentary rocks are not synchronous with metamorphic events under the area that is the source of detrital sediments. If this is true, we should stop trying to associate stratigraphically determined names such as Taconic, Acadian, or Appalachian with metamorphic events identified by isotopic age measurements.

H. FAUL (*United States Geological Survey, Washington, D.C.*): We have a series of events in the Appalachians that seem to be clear-cut and then we have other mixed events that at the moment we do not quite understand.

In Europe, we also have a number of "Hercynian" events. We find 320 m.y. in the Vosges, France, Schwarzwald, Germany, and Massif Central, France, but no similar number on the Appalachian side. We have a 360 m.y. event on the Appalachian side that does not seem to show up in Europe. I think these are regularities of some interest.



R. ST. J. LAMBERT (*Oxford University, Oxford, England*): With regard to that last point, of course, Sir Edward Bailey once drew a structural map showing the "Hercynian chain" going right across the middle of the Atlantic. There are, of course, 280 m.y. dates on the both sides, as you know. I think most of you are aware that the Northwest Highlands of Scotland contain the "Beekmantown" fauna.

## SUMMARY OF DISCUSSION OF PRE-CAMBRIAN MINERAL AGES FROM THE APPALACHIAN PROVINCE

G. R. Tilton, G. W. Wetherill, G. L. Davis  
*Carnegie Institution of Washington, Washington, D.C.*

Age determination studies have been conducted on rocks from the Pre-Cambrian basement complex of the Appalachian orogenic belt from New York to North Carolina. Evidence for the existence of crystalline rocks with ages of 1000 to 1100 million years (m.y.) has been found at Bear Mountain, N.Y., the New Jersey Highlands, Philadelphia, Pa., Baltimore, Md., Shenandoah National Park in Virginia, and in western North Carolina to eastern Tennessee. This finding indicates that rocks of 1000 to 1100 m.y. age, previously well known in southern Ontario, Canada, extend along the Appalachian belt as far south as North Carolina. These measurements make it improbable that the Appalachian mountains represent a Paleozoic accretion to the continent of North America.

A paper on this work will be published shortly in the *Journal of Geophysical Research*.

## SUMMARY OF DISCUSSION ON AGE MEASUREMENTS ON THE BASEMENT ROCKS OF OHIO

Manuel N. Bass

*Carnegie Institution of Washington, Washington, D.C.*

Rb-Sr measurements on biotite and muscovite from some basement rocks of Ohio samples gave 920 to 970 m.y. confirming their association with the Grenville rocks exposed to the northeast. A sample from near Parkersburg, W.Va., gave about 870 m.y. ( $\lambda_{\text{Rb}} = 1.39 \times 10^{-11}$  years<sup>-1</sup>).

G. W. WETHERILL (*Carnegie Institution of Washington, Washington, D.C.*): I do not wish it to be thought that we have retracted any of our data. In particular, the discrepancy between the potassium-argon and rubidium-strontium ages on the biotites in the Philadelphia-Baltimore gneiss still exists, and it is rather similar to that reported by L. E. Long elsewhere in this monograph. The potassium-argon age is 1000 million years and the rubidium-strontium age in the same sample is 400 m.y. ( $\lambda_{\text{Rb}} = 1.39 \times 10^{-11}$  years<sup>-1</sup>). I still do not understand it, but I believe the analysis is correct.

H. D. HOLLAND (*Princeton University, Princeton, N.J.*): May I ask if Tilton is still worried about the low thorium ages. They are consistent and, on the basis of L. T. Silver's remarks elsewhere in the monograph, I wonder if there might be some intergrowth of uranothorite with some of the zircon grains or something peculiar like that. Has this possibility been considered?

TILTON: We have not done any radioautography. The one thing I could say about the low thorium ages is that they will not go below 350 m.y. in the Spruce Pine area, that is, the pegmatite age. In one of the samples I analyzed from that locality the thorium lead age was exactly 350 m.y., and in others it will go up to 400 or 500 m.y.

In the Baltimore area, my thorium lead ages do not go below 300 m.y. and this again is something like the biotite age in the area, so this is the only comment I have to make on that thorium lead situation.

HOLLAND: Do the rocks analyzed by Bass represent basement and were they clearly from some level below Cambrian or are we just concerned with a different part of the section?

BASS: The word basement is used in many different ways by different people, especially in the oil industry. However, I think that these samples were taken from rock in place, since several hundred feet were penetrated. Furthermore, the differences across the boundary are quite real.

HOLLAND: What ages do you think you are dealing with on the west?

BASS: This gets into speculation, but I think I may get the same ages ultimately that people have been getting in the Ozarks in Arkansas and in the Arbuckles in Oklahoma.

TILTON: I have been reminded now that we acid-washed our zircon, so that uranothorite would not have been present.

HOLLAND: This is not necessarily the case. If you have an intergrowth you would get rid of most of this, but there might be just enough left to give you some trouble.

TILTON: Yes, that would be true.

L. T. SILVER (*California Institute of Technology, Pasadena, Calif.*): Actually it depends on the particular uraninite or thorite. The solubilities of the various thorites that we have encountered vary, so that, for example, in our standard treatment most of the uraninite or thorite is eliminated, but we found some samples that would require longer than normal washes in order to get rid of it. Thus a reduced quantity that still could introduce a partial effect might remain.

S. C. ROBINSON (*Canadian Geological Survey, Ottawa, Canada*): In a number of deposits at Bancroft, Ontario, thorite, not uranothorite, is associated with zircons and, from the little chemistry that has been done on the thorites, I do not think any acid washing is going to eliminate them. If this is present, then I think perhaps the problem might be solved.

## AGE MEASUREMENTS ON THE CUTLER BATHOLITH, ONTARIO, CANADA

G. W. Wetherill

*Carnegie Institution of Washington, Washington, D.C.*

At the time that my associates and I started work in the region in northern Ontario, Canada, intermediate between the 2600-million-year-old basement and the 1000-m.y.-old Grenville rocks, no isotopic age data existed. The work at Massachusetts Institute of Technology (MIT), Cambridge, Mass., started at about the same time.

Our work in this region has largely been confined to the region around Cutler and also around Sudbury. Our measurements at Sudbury, which I shall not report now, are quite similar to those obtained by MIT, the principal difference being that MIT has done much more work in the Sudbury area than we have.

However, conclusions that could be drawn from our Sudbury work are about the same as those obtained by the MIT group except that I should be reluctant to attach too much significance to the high K-Ar ages in this region. Again in the region of Sudbury, we, and I believe the MIT people also, still obtain quite high K-Ar ages in contrast to Rb-Sr ages in the same sample of biotite. This seems to be a regional phenomenon, both here and in the Philadelphia area, and I still think there is a strong possibility that this may be related to inheritance of radiogenic argon, and that it is therefore of rather questionable significance.

Today I shall discuss chiefly age measurements that we have made in the Cutler Granite between Sudbury and Sault St. Marie along the north shore of Lake Huron. This paper actually raises more questions regarding methodology than it answers questions concerning the regional history of this portion of the Canadian Shield. Thus, I shall talk about this as more of a methodological paper and then I shall return to some comment on the meaning of these measurements with regard to historic problems in historical geology.

At the present time one of the principal unsolved problems in geochronology is the interpretation of the results of age measurements in terms of geological processes.

When consistent data have been obtained on a geological unit, it is tempting to interpret this in a very simple way as a time of major crystallization of the unit. In cases of metamorphic rocks, a biotite age is usually interpreted as meaning the time of metamorphism. In cases of igneous plutons, quite commonly the result is interpreted as the time of the intrusion of the rock.

This is probably very true in a great many cases, but whether this assumption is always true and the extent to which it is always true is a matter of considerable importance. There is a growing body of data suggesting that this assumption is not always the correct one, even though it may be valid in many cases.

Our work here on the Cutler Granite is, I believe, relevant to this problem. One of the simplest of geologic relationships is that of a small pegmatite cross-cutting another rock. When such a pegmatite is found within a granite body



and extends into the neighboring schist, it may be concluded that the pegmatite is no older than the granite and the schist.

If the simple assumption just mentioned, namely, that the consistent age data obtained on a granite is really the time of intrusion of the granite, consistent age measurements on minerals in the pegmatite should not be older than those in the granite. However, this is not the case for the minerals from pegmatites cutting the Cutler Granite and, as pointed out by L. T. Aldrich elsewhere in this monograph, his data on Michigan are of a similar nature. As a matter of fact, both in our laboratory and in other laboratories there are a number of examples of this sort. I believe the most complete data at the present time on the Cutler Granite are those contained in the present discussion.

The Cutler granite occurs mainly on a peninsula on the north shore of Lake Huron near the Serpent River on the Serpent River Indian Reservation.

The most recently published geological description of this granite body is that of W. H. Collins. Collins observed that the granite is intrusive into metasediments that he relates to the Sudbury series and, on the basis of less definite evidence obtained by P. Eskola, he further concluded the granite has metamorphosed adjacent Mississagi Quartzite on John Island. Therefore, he groups the granite with Killarney and Eagle Island batholiths as a result of a post-Huronian Late Pre-Cambrian orogeny. As a result of this, the granite has ever since been mapped as the latest Pre-Cambrian granitic rock in the region.

A more recent unpublished work of J. Robertson tends to the view that, while the granite is certainly of post-Sudbury age, it may well represent pre-Huronian basement rather than a rock intrusive into the Huronian.

This information is merely for general orientation. What we are more directly concerned with here is that the Cutler Granite and the Sudbury metasediments are clearly crosscut by pegmatites that are well exposed in road cuts along the main highway near Cutler. On geological grounds, there is no doubt that the pegmatites are actually younger than the metasediments and the granites, although they may be only approximately of the same age as the granite. They may represent apophyses of the granite.

One of these pegmatites is clearly undeformed, and there is no clear evidence of any major deformation, metamorphism, or alteration subsequent to the formation of the granite and the pegmatite. This makes it rather difficult to say in an offhand way that any discrepant ages are obtained as a result of metamorphism. There is no geological evidence for the metamorphism except for some milling of the rock; therefore, if it is metamorphism that we are going to be concerned with here, it is metamorphism of a rather subtle type that may well occur in other places where there is no evidence for metamorphism.

We have collected samples from two pegmatites and from the rocks immediately cut by the pegmatite within, in every case within a few meters of the contact between the granite and the pegmatite. In addition we have several samples of granite from further into the central portion of the granite body where no pegmatites were seen.

For one pegmatite-granite pair the pegmatite muscovite Rb-Sr age of 1775 m.y. ( $\lambda_{\text{Rb}} = 1.39 \times 10^{-11}$  years<sup>-1</sup>) is distinctly and completely outside analyt-

ical error, greater than the concordant Rb-Sr ages on the biotite. The muscovites in the granite as well as the K-Ar age from the pegmatite are intermediate between the Rb-Sr age on the pegmatitic muscovite and the concordant granite biotite age.

Another pegmatite about two miles further down the road was also studied. This pegmatite crosscuts the schist in the Sudbury area. Its relationship to the granite is not observed at this outcrop.

The Rb-Sr ages on two samples of muscovite from the pegmatite as well as feldspar from the pegmatite are all in agreement at approximately 1750 m.y. Biotite from the schist is in not quite as good agreement as the biotite from the granite but still is distinctly lower and the Rb-Sr and K-Ar ages are not greatly different.

Again the K-Ar ages from the pegmatitic muscovite are intermediate between the Rb-Sr ages of the muscovite as well as the Rb-Sr ages of the feldspar and the ages obtained on the granitic biotite.

These two muscovites represent two different occurrences of muscovite within this pegmatite. That designated as fine occurs in plumes of about 1-mm. dimension in contrast to this muscovite designated coarse that occurs in books about 1 cm. square. Also the Rb-Sr ages on these two agree quite satisfactorily, as well as with the feldspar, although there is some discrepancy on the K-Ar age.

The feldspar K-Ar age is distinctly lower. I do not attach too much significance to this. This is in agreement with the great bulk of our experience with K-Ar ages on feldspars, and we have not yet duplicated discrepant findings reported by others elsewhere in this monograph. It may well be that this represents a difference between the sanidine found in these volcanics and these low temperature feldspars with which we have been working for some time.

We also have ages measured on two other samples of the Cutler Granite. All these samples are within three or four miles of each other. Biotite ages of 1300 to 1350 m.y. were obtained by both Rb-Sr and the K-Ar methods. Again in this case the K-Ar age of the muscovite agrees with these other four ages. The Rb-Sr age of the granitic muscovite is intermediate between the Rb-Sr ages obtained on the muscovite and the feldspar from the pegmatite and the ages obtained by both K-Ar and Rb-Sr on the biotites from the granite.

In summary, the four Rb-Sr ages on pegmatite agree with each other quite well. The K-Ar ages on the micas are somewhat depressed and, of course, the feldspar K-Ar age is low. On the other hand, all the biotites agree fairly closely at about 1300 to 1350 m.y.

Thus if we had simply measured biotite ages by Rb-Sr or K-Ar on these rocks, we should have obtained a rather consistent picture and, if we had measured Rb-Sr ages on muscovite and feldspar from the pegmatites, we should also have obtained a consistent picture. The principal difficulty is that these two consistent pictures would not be the same. In one case, we should have concluded the rock was 1750 m.y. old; in other cases we said, "Look at all this agreement indicating that it is 1350 m.y. old."

As I said before, this type of thing has been found elsewhere. It has been found in cases of less complete data in Michigan. It has been found in the

Soviet Union and it has been found all through the Paleozoic. People working on the Paleozoic may well be aware this is not something that is peculiar to the Pre-Cambrian, where all factors are exceedingly complicated, but is something that also occurs in the Paleozoic in the vicinity of Baltimore, Md., and Washington, D.C.

The principal moral of my report might be simply to point out that such data exist and to emphasize the need for understanding the meaning of ages in terms of geological processes, pointing perhaps to work on granitic bodies that are very carefully understood where, on as strong geological grounds as possible, the possibility of later mild metamorphic events can be excluded in order to obtain *a priori* criteria for deciding with data of this sort whether it can be said that this is the time of the intrusion of the granite.

It is, however, possible to make some statements relevant to the interpretation of these data, although the principal reason for presenting them is to show that they exist. Of course, probably the most obvious interpretation that would be given if required would be that the entire granite body, including both the pegmatite and the granite, is really about 1750 or 1800 m.y. old and that, subsequently at 1350 m.y., the whole thing became slightly heated, not enough really to make a metamorphism, but enough to allow a biotite that we might suspect to be less able to retain the daughter products than muscovite to lose these daughter products.

An alternative interpretation, essentially the same thing in so far as these data are concerned, would be that the whole region was hot at approximately 300° C. 1750 and 1350, m.y., possibly due to depth of burial.

Of course, other interpretations could be given. Perhaps one that would come to mind fairly easily might be that in some way the pegmatite, muscovite, and feldspar Rb-Sr ages are high because they inherited some kind of radiogenic strontium. This hypothesis cannot be in any ultimate sense disproved, but it can be shown from the data that this does not occur in a very simple way if this is true.

The reason for this is that some of these pegmatitic minerals have much more common strontium in them than others. In particular, one of the muscovites from the pegmatite contained only 0.02 ppm of common strontium 87, whereas the feldspar from the same pegmatite contained 0.72 ppm of common strontium 87. This feldspar is still over 90 per cent radiogenic, but the muscovite is so radiogenic that the feldspar contains 36 times as much common strontium 87 as does the muscovite.

Therefore if the original strontium inherited by this pegmatite was sufficiently radiogenic to make the pegmatite appear to be 1750 m.y. old, even if it was only 1350 m.y. old and, if the same kind of common strontium were inherited by the other muscovite samples as well as by the feldspar samples, all these other samples would have grossly negative ages.

Thus this simple idea of a primary radiogenic strontium inherited by all of the pegmatite minerals does not work. If an explanation in this direction were desired, it would have to be said that a different isotopic composition of primary radiogenic strontium was inherited by every one of these pegmatite minerals that, nevertheless, resulted accidentally in the agreement of these ages around 1750 m.y.

It would also have to be said that the primary strontium 87/88 ratio of this most radiogenic muscovite was 9 instead of the average value of about 0.084, which is more radiogenic than the strontium found in any rock I know.

I shall accordingly not say anything more about the interpretation.

With regard to the regional geology: if we take what I think is the more likely alternative that the whole business, the pegmatite as well as the granite is about 1750 to 1800 m.y. old in spite of the fact that we have no evidence for this hypothetical process that caused this kind of agreement at 1350 m.y.; it implies that the Sudbury series of rocks in this region is greater than approximately 1750 or 1800 m.y., and, if the opinion of W. H. Collins that these rocks also intrude the Mississagi Quartzite is correct, then this same limit of around 1800 m.y. applies to the age of this lower Huronian formation in this region.

On the other hand, if the Cutler Granite is part of the pre-Huronian basement, the Huronian sedimentary rocks are probably younger than 1800 m.y. Since there are relatively few massive granite bodies in the region of the north shore of Lake Huron having known relationships to the strata, it would be of some value toward establishing a Pre-Cambrian chronology of this region if a relationship of the Cutler Granite to the Mississagi could be established by field observations. This would probably require investigations of the Cutler-Huronian contact on the islands in Lake Huron to the south since the contact in the north is obscured by a major fault zone.

The only other thing I could say (in agreement with the data presented elsewhere in this monograph by H. W. Fairbairn based on data in the Sudbury region and also on some other granitic data on the north shore) is that, if the Cutler batholith is related to an orogenic belt, the age of this orogenic belt is distinctly older than that of the 1000-m.y.-old granites of the adjacent Grenville orogenic belt and accordingly does not represent a very late Pre-Cambrian orogenic belt as the rock is conventionally mapped.

### *Discussion of the Paper*

G. H. CURTIS (*University of California, Berkeley, Calif.*): In support of Wetherill's thesis, my associates and I have dated in New Zealand basement rocks along the Alpine fault. The same phenomenon shows up there, the pegmatites being around 77 m.y. old, the schist near the fault being, from the dates we get, 4 to 15 million years.

Here, rather perhaps than heating, although this is certainly a possibility, is the possibility of deformation of the schist also. The schists outcrop elsewhere and are known to be at least pre-Upper Cretaceous, so they have existed that long. Thus the 4- to 15-m.y.-age is certainly invalid. However, whether the schists have been heated—Turner is of the opinion that they have been heated—they have been deeply buried and therefore should have been heated. It is difficult for me to understand why, if they have been deeply buried, the pegmatites did not lose their argon. However they have also been extensively deformed in post-Oligocene time. The Oligocene series, which is not schistose, has been intensively folded, so my suggestion would be that perhaps the granite has been slightly deformed.

Our experience at Berkeley has been that if a mineral lattice is in any way altered or deformed, rapid loss of argon results.



WETHERILL: In our case, however, the pegmatite is completely straight, apparently undeformed. There is some milling observable in thin sections, but this is no greater than that observed in many rocks called good granites, and commonly, if they were in the Appalachians, would be dated with great confidence.

H. W. FAIRBAIRN (*Massachusetts Institute of Technology, Cambridge, Mass.*):

I think it would be extremely valuable for the sake of North Shore geology that whole rock analysis should be tried on the Cutler because the basement rocks under the Huronian beds are already at least 2200 m.y. old and, if this is 1700 m.y., it would be interesting because there is no definite evidence of a granite of that age at the moment.

WETHERILL: This may be a good idea; on the other hand I can say that, if there is any primary radiogenic strontium in the granite, it is not in the apatite. The strontium in the apatite from the granite is completely normal. It may be as much as 1 per cent radiogenic, but this is within experimental error in Michigan.

B. J. GILETTI (*Oxford University, Oxford, England*): I shall just point out another example of the discrepancy between muscovite, biotite, and feldspar that is slightly more striking than this. This is in the Teton Range in Wyoming where it has been observed that a muscovite gives a 2500-m.y. age. This muscovite is a book muscovite in a pegmatite that is cutting biotite-bearing gneiss, and biotite in the gneiss gives a 1300-m.y. age, all by Rb-Sr ( $\lambda_{\text{Rb}} = 1.47 \times 10^{-11} \text{ years}^{-1}$ ).

Incidentally, the potassium feldspar associated with the muscovite in the pegmatite gives a 1900-m.y. age. There is no question in this case about the inheritance of an abnormal common strontium, because total normal strontium in the muscovite of about 2 ppm is obtained.

S. C. ROBINSON (*Canadian Geological Survey, Ottawa, Canada*): My associates and I have found less sharply defined evidence of the same thing in the Bancroft area of Ontario, where biotite from pegmatites and unfoliated granites gives older K-Ar ages than biotites from foliated granites and from the surrounding limy metamorphic rocks.

It is suggested that biotites in the more competent and more refractory rocks, have been better protected from subsequent dynamic and thermal metamorphism than biotites in the less competent rocks. Loss of argon in biotites in competent rocks has therefore been less and their ages are apparently older.

I have one other question that I should like to ask Wetherill. Where Rb-Sr ages are greater than K-Ar ages, is it possible that this is due to preferential loss of rubidium by leaching? I understand from our friends in geochemistry that rubidium, like cesium, is very soluble in ground waters.

WETHERILL: You think the pegmatite ages may have been raised by loss of rubidium. I have no data to exclude this except that then the agreement of the 1750 m.y. would have to be regarded as coincidental, particularly in view of the rather different rubidium concentration in the different minerals, even between the two different samples of muscovite.

J. L. KULP (*Columbia University, New York, N.Y.*): At low temperatures rubidium and cesium are more strongly absorbed than potassium on silicate



surfaces, so that I do not think relative loss of rubidium is a possibility. If anything, rubidium would be enriched relative to potassium on the silicate surface.

Also may I emphasize the fact that, in looking at the biotite ages given by a number of contributors to this publication, occasionally there occurred an age that was low by about 10 or 15 per cent, just an odd biotite age. It was unaccompanied by any other age.

Several workers report occasional K-Ar ages on biotite that were lower than associated muscovites. They suggested that this might be due to some subsequent metamorphism. May I repeat that our base exchange experiments showed that it is possible to get 10 or 15 per cent lowering of the  $\text{Ar}^{40}/\text{K}^{40}$  ratio from this process, so it is not necessary to appeal to anything else for ground water. One indication that such a process has occurred is a low potassium content of the biotite.

P. W. GAST (*University of Minnesota, Minneapolis, Minn.*): I was hoping B. J. Giletti would mention something of the work that he has done in the Little Belt Mountains in Montana, and this is in connection with a point that there is no evidence of any metamorphism in some of these places.

In the Little Belt Mountains there is a profound unconformity between the overlying unmetamorphosed sandstone and the crystalline rocks underneath them. Two biotites from the basement rocks proved to be 50 and 200 m.y. old by Rb-Sr but the basement is at least 2400 m.y. old as determined by zircons and Rb-Sr on feldspar.

There are rhyolite intrusives nearby that could have caused a slight temperature rise but no metamorphism. This appears to account for the loss of the argon, but there is no other observable effect on the crystallines or the associated sandstone.

Thus here is an example of no recognizable metamorphism accompanied by the low ages.

P. E. DAMON (*University of Arizona, Tucson, Ariz.*): There is another anomaly, that between sanidine and the other feldspars. I read recently a paper—I forget the author—on the effect of “perthitization” on the argon retentivity, and the conclusion of this paper was that there was a direct relationship between the degree of “perthitization” and argon loss. I do not know whether others have found a similar relationship but, for the record, this is in Geokhymia.

P. M. JEFFERY (*The University of Western Australia, Nedlands, Australia*): I shall just comment on the matter of the total rock analysis mentioned elsewhere in this monograph. I doubt total rock ages that are obtained by taking a single total rock sample and determining the rubidium and strontium in it. Normally, there is a high abundance of common strontium in the rock with the result that the value of the strontium 87/86 initial ratio that is selected becomes a critical question. For total rock analyses multiple sampling of the rock, using samples with different gradients, is essential.

There is actually an example where, if the normally accepted value of the strontium is used, quite an old age is obtained, whereas this particular rock is known to be much younger.

## SUMMARY OF DISCUSSION OF MINERAL AGE MEASUREMENTS IN THE CANADIAN SHIELD

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Rb-Sr, K-Ar, U-Pb, and Th-Pb ages have been determined by the method of isotope dilution on suitable minerals from a number of rocks in southern Ontario, Canada and northern Michigan. The results of these measurements may be summarized as follows:

(1) Rocks at least 2500 million years (m.y.) old exist across the entire province of Ontario and extend as far south as Iron Mountain, Michigan.

(2) Metamorphic events in northern Michigan have affected the ages of zircons, micas, and feldspars in different ways, so that the complete analysis of events is as yet imprudent.

(3) Evidence of younger metamorphic events at 1800, 1400, and 1100 m.y. have been found in Iron and Dickinson Counties of Michigan.

(4) There is no a priori reason to believe that any region on the earth has not been subjected to metamorphic events similar to those encountered in this and other areas to be discussed. It seems, therefore, somewhat premature to make stratigraphic correlations on the basis of age measurements by a single method at this point except as an exercise of the imagination.

# SUMMARY OF DISCUSSION OF AGE INVESTIGATIONS AT SUDBURY, ONTARIO, CANADA\*

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Age investigations of minerals in a wide variety of rocks from Sudbury, Ontario, have been carried out in laboratories at Massachusetts Institute of Technology, Carnegie Institution of Washington, Washington, D.C., and University of Toronto, Ontario, Canada. For the most part the data obtained by three independent methods on suitable coexisting minerals fail to give either compatible intermineral or compatible intermethod results. For Rb-Sr the discrepancies are probably related to recrystallization resulting from diastrophism of the area, whereby biotite, and to a lesser extent K-feldspar, give

TABLE 1  
RUBIDIUM-STRONTIUM ANALYSIS OF WHOLE ROCK SAMPLES\*

	Biotite	K-feldspar	Whole rock
Copper cliff "rhyolite"	1310 m.y.	1985 m.y.	2215 m.y.
Creighton granite	1275 m.y.	1490 m.y.	2055 m.y.

\*  $\lambda_{\text{Rb}} = 1.47 \times 10^{-11}$  years<sup>-1</sup>.

'ages' younger than the absolute age. Following the lead of Compston and Jeffery (1959), Rb-Sr analysis of whole rock samples is now underway wherever the Rb/Sr ratio is sufficiently favorable, with two completed results (TABLE 1).

These whole rock ages are believed to be more realistic estimates of absolute age than the mineral ages. It is hoped that further work on whole rock samples will show reasonably close correlation with the assumed igneous sequence and that the K-feldspar and biotite analytical data will provide evidence of the approximate time of subsequent orogeny.

## Reference

COMPSTON, W. & P. M. JEFFERY. 1959. Anomalous common Sr in granite. *Nature*, **184**: 1792, 1793.

\* By prior agreement with the Geological Association of Canada, Toronto, Canada, the investigation summarized here has been submitted as a manuscript for publication in the *Transactions* of that organization, under the authorship of H. W. Fairbairn, P. M. Hurley and W. H. Pinson.

## SUMMARY OF DISCUSSION OF PRE-CAMBRIAN OF CENTRAL WISCONSIN

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According to Weidman (1907), the oldest rocks of central Wisconsin are a group of biotite schists and gneisses of medium to high grade. Weidman uncertainly regarded a group of slates and low to medium grade two-mica schists as younger. The younger group attains high-grade metamorphism only in aureoles adjacent to still younger igneous rocks. Both groups of metamorphic rocks yield only metamorphic ages indicative of more than one event. Their age ranges overlap almost completely. The ages, therefore, do not resolve the question of relative age of the two groups. The oldest age measured is 1900 million years (m.y.) ( $\lambda_{\text{Rb}} = 1.39 \times 10^{-11} \text{ years}^{-1}$ ).

The ages of massive igneous rocks are variable. The greatest concentration of Rb-Sr ages indicates extensive granite emplacement about 1400 m.y. ago, a time at which similar emplacement occurred in Missouri. Rb-Sr ages of 1500 m.y. for the Wausau, Wisconsin syenite complex suggest it is older than the granites, but this requires further work for confirmation.

The scattered ages significantly less than 1400 m.y. cannot be assigned at present to a specific event. They may be due to a renewal or continuation of igneous activity on a reduced scale.

The massive igneous rocks apparently did not attend regional metamorphism, so the ages of the granites cannot be taken to date an orogeny.

### *Reference*

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# CANADIAN SHIELD AGE PROGRAM OF THE GEOLOGICAL SURVEY OF CANADA\*

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## *Introduction*

The Geological Survey of Canada has recently commenced an extensive program of K-Ar age determination in the Canadian Shield, and it may be of interest to summarize the results to date and to outline the general program. Full details will soon be available in the first of a series of annual reports on age determination.

The Survey, since its formation about 120 years ago, has been endeavoring to work out a satisfactory geochronological classification of Pre-Cambrian rocks of the Shield. Until recently, the best that could be done was to attempt to build up a relative time scale based primarily on superposition of strata. For correlation between regions, geologists had nothing better to rely upon than unsatisfactory criteria such as lithological similarity, comparison of sequences, relationship to unconformities, and relationship to intrusions. A number of geochronologic units of series and system rank gradually came into use, some only locally, others such as Keewatin and Huronian being extended by some geologists interregionally. For Shield-wide correlation a dual classification of Pre-Cambrian time, Archean and Proterozoic, was eventually adopted by the survey and is in use today. This involves long-range correlation on admittedly unsatisfactory evidence. It is as yet too soon to say how well or how poorly the geologists have done. With the development of new methods and techniques based on the radioactive decay of certain isotopes, it became possible to determine ages in terms of years and former work must now be re-evaluated in light of the new data being obtained.

With the aid of the new means of dating it is expected that time-stratigraphic principles can now be applied in the Pre-Cambrian with greater hope for success than formerly. Principles of time classification were developed in the fossiliferous part of the geological column and the time scale was based primarily on sedimentary strata, the intrusive rocks playing an insignificant role. In the Pre-Cambrian, on the other hand, the igneous rocks are more readily and more directly dated, and it is felt that these, and more especially the intrusive igneous rocks, may play an increasingly important part in geochronology. It seems natural and logical that we should study the possibilities of establishing time-stratigraphic units of intrusive igneous rocks with the thought that they may eventually form the main frameworks for Pre-Cambrian geochronology. Assemblages of sedimentary and volcanic rocks will be important also but these, excepting sediments containing a suitable authigenic mineral or volcanic rocks containing a suitable unmetamorphosed primary mineral, can only be bracketed between maximum and minimum age limits. The concept of a type section or type locality for a stratigraphic unit has been rather poorly handled by Pre-

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Cambrian geologists in the past and it is felt that, as we are now embarking on a new approach to geochronology, we should be more careful about choosing and defining type areas and more cautious about extending time units geographically beyond the type localities. It is only the isotope ratio in a mineral that is tangible and measurable. The age of a rock is inferred from the isotope ratio and the interpretation is subject to change from time to time, but the true age of a rock at a type locality does not vary. The rock at a type locality thus serves as a standard control for a time-stratigraphic unit; its apparent age can be changed and mistakes in correlation can be corrected without upsetting the stratigraphic nomenclature.

### *Age Program of the Geological Survey*

The absolute age program of the Geological Survey of Canada started with the work of Ellsworth who published his findings, based on chemical analysis for total U, Th, and Pb in 1932.<sup>1</sup> Quirke and Collins<sup>2</sup> were the first survey geologists to appreciate the implications of the new method as applied toward the solution of a particular geological problem. When isotopic methods became available, this work was continued and at present we are using chiefly the K-Ar method on micas.

Approximately 100 K-Ar age determinations have been carried out in the laboratories of the Geological Survey of Canada during the past 18 months. In the early work, micaceous minerals were fused with sodium hydroxide flux and the released gases were treated with magnesium perchlorate, hot copper oxide, and titanium sponge. Recently, a high frequency induction heating unit has been installed and all samples are now fused in alundum crucibles without the addition of a flux. The new unit is employed in conjunction with a high vacuum line embodying Alpert-type metal valves. The released gases are purified by treatment with hot copper oxide and titanium sponge.

With the introduction of high frequency induction heating equipment, a marked reduction in the amount of atmospheric argon contamination has been observed. It now appears that at least 90 per cent of previous contamination originated in the sodium hydroxide flux, in spite of the fact that every precaution was taken to ensure preliminary out-gassing of the flux before mixing with the sample material.

Isotope dilution techniques are employed to determine the argon-40 content and all isotopic analyses are carried out on a 10-inch radius, 90° Nier-type mass spectrometer. The ages reported have been calculated using the following constants:

$$\lambda = 5.30 \times 10^{-10} \text{ yr.}^{-1}$$

and

$$\lambda e = 0.585 \times 10^{-10} \text{ yr.}^{-1}$$

The potassium content is determined on a Beckman D.U. flame spectrophotometer on a neutral sulfate solution prepared by decomposition of the sample with HF and H<sub>2</sub>SO<sub>4</sub>, ignition to decompose R<sub>2</sub>O<sub>3</sub> sulfates, and leaching with water.<sup>3</sup>

Petrological and mineralogical studies are made on all rock samples submitted for dating. Mica concentrates are examined by microscope and semiquantitative X-ray diffraction methods to ensure freedom from alteration products and a normal standard of purity of over 95 per cent.

To date, age determinations have been based on K/Ar ratios in micaceous minerals and Pb/U and Pb/Th ratios in uraniferous minerals. With the completion of a new solid source mass spectrometer age measurements based on the Rb/Sr ratio will be undertaken. In addition, plans are being made to determine isotopic lead ages on zircons.

Our study of age determination by the K-Ar method has developed through three stages: first, a comparison with uraninite ages; second, a detailed study of a small batholith and its associated rocks; and, third, an age reconnaissance of Canada, chiefly in the Canadian Shield.

The first step was undertaken by S. C. Robinson, R. J. Traill, and R. K. Wanless and was designed to test the reliability of K-Ar ages as compared with uraninite or thorinite as standards. Only those that gave approximately concordant ages from at least three of the ratios,  $\text{Pb}^{206}/\text{U}^{238}$ ,  $\text{Pb}^{207}/\text{U}^{235}$ ,  $\text{Pb}^{207}/\text{Pb}^{206}$ , and  $\text{Pb}^{208}/\text{Th}^{232}$ , were considered to be sufficiently reliable to be used as a standard. The micas used for K-Ar ages were unaltered. The study included six examples in which these conditions were met and in which the two minerals occurred in the same body of rock and were considered on geological evidence to have crystallized at about the same time. As shown in TABLE 1, the agreement between phlogopite and uraninite or thorinite is good. In one example the ages for biotite and uraninite are virtually identical but, as a rule, the biotite ages and the one muscovite age are somewhat younger than the corresponding uraninite. They differ by only about 5 per cent on the average and, on the whole, the results are gratifying.

The second stage of our program was a study of K-Ar ages on micas from a small batholith, its pegmatites, and its surrounding metamorphic rocks, and was undertaken by N. J. Snelling.<sup>4</sup> The Preissac-Lacorne batholith of western Quebec was chosen because detailed geological studies had previously been undertaken there. The geological work was done by K. R. Dawson (in preparation), who concluded that various facies of the batholith, its associated pegmatite dykes, and the metamorphism of surrounding sedimentary and volcanic rocks are closely related to one another in time of origin. It was expected, therefore, that micas from the several rock types would be almost the same age. However, the K-Ar ages, as shown in TABLE 2, vary considerably and in the extreme case, as between 2735 m.y. for muscovite (K-Ar 30) and 2310 m.y. for biotite (K-Ar 32), differ by 425 m.y. or about 18 per cent, which is greater than the analytical error. The discrepancies, however, are not haphazard, for the lepidolite and muscovite ages agree reasonably well with one another and the biotite ages are all younger. The muscovite (K-Ar 33, 2630 m.y.) and the biotite (K-Ar 32, 2310 m.y.) are from the same sample of granitic rock but differ in calculated age by 320 m.y. The average muscovite from pegmatites (2637 m.y.) is 230 m.y. older than the average biotite (2407 m.y.) from granitic rocks that the pegmatites cut. Such results are geologically unreasonable and, obviously, cannot all be the true age of crystallization. By adding a factor of 10 per cent to the average biotite ages, it is found that the discrepancies prac-

TABLE 1  
POTASSIUM-ARGON AGES ON MICA COMPARED WITH COEVAL URANINITE AND THORIANITE AGES

Sample No.	Locality	Name of rock	Mineral	Age in millions of years					K <sup>40</sup> -Ar <sup>40</sup>
				Pb <sup>207</sup> -Pb <sup>208</sup>	U <sup>235</sup> -Pb <sup>207</sup>	U <sup>238</sup> -Pb <sup>206</sup>	Th <sup>232</sup> -Pb <sup>206</sup>	Average	
A-D 46 K-Ar 8	45°01'N., 78°12'W. 45°01'N., 78°12'W.	Calcite-fluorite vein Calcite-fluorite vein	Uraninite Phlogopite	1040	1060	1085	1105	1070 ± 25	1060 ± 65
A-D 45 K-Ar 9	45°07'N., 77°47'W. 45°07'N., 77°47'W.	Skarn Skarn	Thorianite Phlogopite	1040	1040	1060	1025	1040 ± 10	1085 ± 65
A-D 242	45°03'N., 78°10'W.		Uraninite	980	1000	1000	1000	995 ± 10	
A-D 241 K-Ar 7	45°03'N., 78°10'W. 45°03'N., 78°10'W.	{Pegmatitic Segregation in skarn	Uraninite Biotite	1025	945	920	910	950 ± 40	910 ± 55
A-D 243 K-Ar 11	45°10'N., 77°44'W. 45°10'N., 77°44'W.	Pegmatite Pegmatite	Thorianite Biotite	990	970	955	940	965 ± 20	925 ± 55
A-D 90 K-Ar 15 K-Ar 14	47°46'N., 70°24'W. 47°46'N., 70°24'W. 47°46'N., 70°24'W.	Pegmatite Pegmatite Pegmatite	Uraninite Muscovite Biotite	1020	980	975	*	990 ± 20	925 ± 55 935 ± 55
A-D 43 K-Ar 24	59°35'N., 108°17'W. 59°35'N., 108°17'W.	Pegmatite Pegmatite	Uraninite Biotite	1925	1945	2000	2120	2000 ± 65	2015 ± 100

\* Thorium content too low (0.09 %) for reliable age calculation.

tically disappear. This does not mean that a similar correction can necessarily be added to biotite ages in other areas where conditions of crystallization or subsequent history may have been different. It is hoped that research may eventually point to the fundamental reasons for such discrepant ages. This study has demonstrated the advisability of obtaining K-Ar ages on both muscovite and biotite from the same sample, that the average of several samples from the same rock are undoubtedly better than only one, and that proper interpretation requires knowledge of the geological setting. Checks by the Rb-Sr method would have helped in the interpretation. In spite of the apparent discrepancies, the K-Ar ages on micas are generally of the right order of magnitude and, considering the great length of Pre-Cambrian time, can be

TABLE 2  
POTASSIUM-ARGON AGES ON MICAS FROM THE PREISSAC-LACORNE BATHOLITH AND ITS ASSOCIATE PEGMATITE AND SURROUNDING METAMORPHIC ROCKS\*

Sample No.	Name of rock	Mineral	Age (millions of years)		
			K-Ar	Average	Average + 10%
K-Ar 29	Pegmatite	Lepidolite	2735	2735	2637
K-Ar 30	Same sample as K-Ar 29	Muscovite	2735		
K-Ar 25	Pegmatite	Muscovite	2540		
K-Ar 33	Granodiorite	Muscovite	2610 2650	2630	2630
K-Ar 32	Same sample as K-Ar 33	Biotite	2240 2285 2405		
K-Ar 45	Granodiorite	Biotite	2500		
K-Ar 51	Quartz diorite	Biotite	2450	2407	2647
K-Ar 50	Granodiorite	Biotite	2370		
K-Ar 44	Schist, same locality as K-Ar 50	Biotite	2455 2310	2382	2620

\* Adapted from N. J. Snelling (in preparation).

used with considerable confidence in making broad distinctions or approximate correlations.

We therefore embarked on the third stage of our program: an age reconnaissance of the Canadian Shield. Accordingly, a large number of samples were collected over a substantial part of the Shield, as shown in FIGURE 1. Some major gaps remain to be filled in and we hope to do this in the near future. In choosing the samples we were guided, for the most part, by geological maps, and each sample was collected either as representative of a large area or to throw light on some particular problem. The immediate objective is to assist in defining and outlining orogenic provinces for a proposed tectonic map of Canada. For this purpose we are interested primarily in obtaining ages of metamorphism and intrusions and most of the samples are of high grade, thoroughly recrystallized metamorphic rocks and of unmetamorphosed granitic



rocks and pegmatites. Biotite will be the mineral most commonly dated, but it will be possible to compare the ages of biotite and muscovite in a fairly large number of the samples. We have not yet had time to produce more than a few ages from this material, but FIGURE 2 shows the localities of samples for which we have already carried out age determinations. At this early stage we cannot add much new information on the boundaries or ages of the structural provinces already depicted by Gill,<sup>5</sup> Wilson,<sup>6</sup> and Cummings *et al.*<sup>7</sup> The mineral provinces of Gastil<sup>8</sup> are less closely tied in with the geology. Some



FIGURE 1. Localities in Canada where samples have been collected by the Geological Survey of Canada for age determinations.

changes are indicated and, in FIGURE 2, we have altered the boundaries somewhat to conform with new geological information and age data. For example, the Superior province may now be extended on better evidence well up into northern Quebec; the boundary between the Churchill and Slave (Yellowknife) provinces swings north from near the east end of Great Slave Lake; and the Churchill province may be extended northeast through the southern District of Keewatin and, possibly, into southern Baffin Island. We have not yet compiled and evaluated all the published data, but some tentative generalizations on the ages of orogenies in the various provinces may be made. The Slave and Superior provinces were involved in the oldest orogenies, generally older than 2000 m.y. In the Churchill province the age of metamorphism and





is, the two ages in the Superior province were expected to be somewhat older and to fall more in line with the common age of 2400 to 2700 for that province, while the 1695 and 1270 ages are older than the common age of about 800 to 1000 in the Grenville province. Although the ages found may be the true ages of crystallization of the biotites, it seems more probable that this mineral in each province was affected in some way by its proximity to the other province. Obviously more information and research is required.

Although the study of orogenies is the main and immediate purpose of our reconnaissance program, the results are expected to contribute toward a solution of the much more difficult problem of geochronology of Pre-Cambrian stratigraphic units. It is not yet possible to work out a natural time classification that is best suited to the whole of the Shield, but we have a few interesting results. For example, the rocks of the Labrador trough, which are considered to be Proterozoic, fall within the apparent limits of 2365 and 1935 to 1875 m.y.; they lie unconformably on rocks of the Superior province. Biotite from the Proterozoic Dubawnt porphyry, a flat-lying, unmetamorphosed volcanic rock, gave an age of 1515 m.y.; this rock lies unconformably on rocks of the Churchill province. The Abitibi (Keewatin?), Pontiac, Rice Lake, Yellowknife, and other groups have long been classed as Archean and more than 2000 m.y. old; these have been involved in the orogenies that affected the Superior and Slave provinces. At the moment a twofold division at about 2000 m.y. seems to best fit our present classification into Archean and Proterozoic, but it is not yet known whether this horizon will be the most practical for dividing the Shield as a whole. The difficulty is that it has not yet been possible to trace this horizon through the Churchill and Grenville provinces, both of which have been involved in younger orogenies. However, geological evidence suggests that rocks as old as Archean may be present in these provinces, and a satisfactory solution may eventually be found by considering both geological and absolute age methods.

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### Discussion of the Paper

P. M. HURLEY (*Massachusetts Institute of Technology, Cambridge, Mass.*): I shall register a protest at this point on the use of the terms Proterozoic and

Archean and on drawing a line between the two at a certain age, just to have it on the record.

I do not think we are ready for it yet, because this is now a world-wide question.

H. FAUL (*United States Geological Survey, Washington, D.C.*): May I ask a question in the same vein. Does this line exist?

STOCKWELL: At the moment, we have done no more than attempt to classify some of the rocks of the Canadian Shield. The world-wide problem is a very important one and I think the way to deal with it is step by step. I do not understand why there should be an objection to the words Archean and Proterozoic.

HURLEY: Perhaps I should explain my comment. The terms Archean and Proterozoic have developed strong connotations in the literature. Proterozoic tends to be used as a structural as well as an age term, and elsewhere we find it applying to relatively flat-lying Pre-Cambrian formations forming basins in an Archean complex. For example, in Australia the term Proterozoic has been applied to large Pre-Cambrian basin structures in the Northern Territory before any age measurements were made on these, as reported elsewhere in this monograph. I think it is also confusing to set actual age limits on these terms at this time. However, I certainly do not wish to debate this point at this time, but simply to register a question concerning the use of these terms.

STOCKWELL: I think, if I may add a few more comments, there has been much misunderstanding of the terms Archean and Proterozoic. They are very definitely defined, and the dividing line is at present put at the time of beginning of deposition of the Huronian rocks in the area north of Lake Huron. Structure, degree of metamorphism, relationship to intrusions, and other considerations are used as criteria for correlating rocks of other areas with those of the type locality, but form no part of the definition.

## SUMMARY OF DISCUSSION OF PRE-CAMBRIAN GEOCHRONOLOGY OF MINNESOTA AND ADJACENT AREAS

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Radioactivity dating of a large number of samples by the  $K^{40}$ - $Ar^{40}$  and the  $Rb^{87}$ - $Sr^{87}$  methods favors a threefold division of the Pre-Cambrian rocks of Minnesota and adjacent areas; however, considerable revision of the threefold classification used by the Minnesota Geological Survey is suggested. The time boundary between Early and Middle Pre-Cambrian is placed at 2.5 billion years (b.y.), and between Middle and Late Pre-Cambrian at 1.7 b.y. These boundaries are marked by major orogenies, the Algoman and the Penokean.

The Laurentian orogeny is included within the Early Pre-Cambrian and is relegated to a secondary role. The magnitude of the mountain building during the Penokean orogeny, at approximately 1.7 b.y., was not fully appreciated in the past. The Grenville orogeny apparently was not of a mountain-building scale in the Lake Superior region, but it is recognized in lesser structural disturbances and in the igneous activity of the Middle Keweenawan of Minnesota, Ontario, Wisconsin, and Michigan, 1.2 to 1.0 b.y.

The Couitchiching, Keewatin, and Knife Lake (Seine) groups are assigned to the Early Pre-Cambrian. The Animikie group of Ontario and Minnesota and the iron formations and related sedimentary rocks of Wisconsin and Michigan formerly assigned to the Huronian are Middle Pre-Cambrian. The Sioux formation of Minnesota, South Dakota, and Iowa is Late Pre-Cambrian and probably pre-Grenville. The Fond du Lac and Hinckley formations of Minnesota and their correlatives and related rocks in Wisconsin and in Michigan are post-Grenville.

A complete account of this work, entitled "Precambrian Geology and Geochronology of Minnesota" is in press and will appear as Bulletin 41 of the *Minnesota Geological Survey*, University of Minnesota Press, Minneapolis, Minn.

# THE AGE OF THE BASEMENT ROCKS OF THE COLORADO PLATEAU AND ADJACENT AREAS\*

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## *Pre-Cambrian Geology*

The area under consideration, adjacent to and encompassing the Colorado Plateau in the United States, includes the Southern Rocky Mountain province of Wyoming, Colorado, and New Mexico, and the basin and range province of Arizona and New Mexico. The front range, which extends from central Wyoming through Colorado into New Mexico, is the largest continuous area of Pre-Cambrian rock within the region. Thousands of square miles of Pre-Cambrian rock outcrop in the central highlands and basin and range province of Arizona. However, the age of much of the Arizona Pre-Cambrian has been inferred rather than demonstrated. Large areas are directly overlapped by Tertiary volcanics and alluvium. Early Arizona geologists, through lack of better criteria, classified all schists and gneisses as older Pre-Cambrian. Of course, many geologists have questioned the validity and usefulness of such a classification. The present demonstration, by geochemical dating, of a Cretaceous-Tertiary age for some rocks previously classified as Pre-Cambrian will not come as a great surprise to those geologists who are familiar with the problem. However, the Pre-Cambrian age of other formations has been confirmed by geochemical dating, and there is no doubt concerning the age of large areas overlain by younger Pre-Cambrian or Paleozoic sediments.

Pre-Cambrian rocks are exposed north of the Colorado Plateau in the Uinta range of northeastern Utah, the Wasatch range in the Salt Lake district, and within the basin and range province of western Utah and eastern Nevada. Unfortunately, little or no geochemical dating data are available for this area at this time.

Early workers divided the Pre-Cambrian of the southwestern states into two systems, the Archaean and Algonkian or Proterozoic. This implies a correlation with the Cryptozoic rocks of the Canadian shield, which has not been established. Consequently, the noncommittal terminology, Older and Younger Pre-Cambrian, advocated by Butler and Wilson (1938, p. 11), has been generally adopted in Arizona (Anderson, 1951, p. 1333; Lance, 1958, p. 66). The general geology of the Pre-Cambrian rocks of northern Arizona has

\* Geochronology Laboratories, University of Arizona, Contribution No. 38; Lamont Geological Observatory Contribution No. 459.

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been reviewed by Lance (1958). Regional correlation of the Older Pre-Cambrian rocks has been recently discussed by Anderson and Creasey (1958, p. 44).

The two systems of Pre-Cambrian rock are clearly exposed along the bottom of the Grand Canyon in Arizona. The crystalline complex forming the inner walls of the Granite Gorge of Grand Canyon has been called the Vishnu Series (Campbell and Maxson, 1938). The Vishnu Series consists of 25,000 feet of metasediments, originally fine grained argillaceous sandstone and sandy shale, now metamorphosed to quartzite, sericite quartzite, and quartz-mica schist. In addition, they recognized a sequence of basaltic flows and tuffs with relict pillow and amygdaloidal structures, which are now metamorphosed to amphibolite. Migmatization is common and the entire Older Pre-Cambrian sequence is extensively folded and faulted and intruded by quartz diorite, aplite, and granitic pegmatite.

The Younger Pre-Cambrian of the Grand Canyon, the Grand Canyon series, consists of about 12,000 feet of relatively clean and unmetamorphosed sandstone, shale, and limestone. The Unkar group (lower Younger Pre-Cambrian) is intercalated with about 900 feet of basalt and intruded by diabase dikes. Following the deposition of the Grand Canyon series, the Grand Canyon disturbance caused faulting and gentle folding. Consequently, the Paleozoic section unconformably overlies the Younger Pre-Cambrian.

The Vishnu Series has been correlated with very similar rocks of central and southern Arizona, the Yavapai and Pinal series, respectively. The Younger Pre-Cambrian Apache group, consisting of up to about 1500 feet of sediments similar to the Grand Canyon series, unconformably overlies the Older Pre-Cambrian from central to southern Arizona. The Apache group is capped by a basalt flow and intruded by diabase sills and feeder dikes.

Wilson (1939) was first to point out the prevailing northeast trend of folds and schistosity of the Older Pre-Cambrian of Central Arizona. He concluded that "the principal structures in the Older Pre-Cambrian rocks resulted from one profound crustal disturbance—the Mazatzal Revolution—which took place after the Mazatzal quartzite, and long before the Apache strata were laid down. Marked by intense northwestward compression and culminating with the batholithic invasion of . . . granite . . . , this revolution doubtlessly gave rise to a huge range . . ."

The same predominant, Older Pre-Cambrian structural trends are observed throughout Arizona. For example, Thomas (1949, p. 668) in his study of the Pre-Cambrian Cerbat complex north of Kingman, Ariz., states: "all the folding has a uniform northeast axial trend." Anderson and Creasey (1958, p. 62) observe that: "Throughout Arizona, Anderson (1951) recognized a broad similarity in the structure of the Older Pre-Cambrian rocks. Folds trending northward or northeastward occur in the Little Dragoon and Mazatzal Mountains and at Bagdad, and similar trends plus northwest trends are present in the Jerome area." Lance (1958, p. 66) summarizes the evidence for the Vishnu Series: "This regional deformation, which Noble and Hunter stated to be the most obvious event in the Archaean history of the area, produced foliation and schistosity with predominant northeast strike and nearly vertical dip, indicating compression from either southeast or northwest." According to Ransome (1919, p. 34), in the Globe and Ray quadrangles, "the prevailing strike of the

schistose cleavage in this and in other schist area is northeast." In describing the Older Pre-Cambrian rocks of the Dragoon quadrangle in Cochise County, Cooper and Silver (1954, p. 1242) state: "The structure is a complex of isoclinal folds, which trend northeast and commonly have steeply overturned limbs and axes." They further conclude (p. 1242): "Most of the Pinal and Yavapai schists of southern and central Arizona probably originated in a major geosynclinal trough whose complete extent is not known. This trough was the orogenic site of Wilson's Mazatzal Revolution." Finally, Gastil (1958, p. 1511) also observes: "The Older Pre-Cambrian rocks of the Diamond Butte quadrangle constitute a northeast-southwest trending belt, nearly surrounded by younger granite."

A similar prevailing northeast trend is observed for the Older Pre-Cambrian in Colorado (King, 1959, p. 99; Mayo, 1958, p. 1169) and in southern Wyoming (Lovering, 1933, p. 273). This prevailing trend suggests to King, "the existence of an ancient mountain structure along the prolongation of those in the southeast part of the Canadian shield." B. S. Butler (1933, pp. 204-209) has pointed out the similarity of both the Younger and Older Pre-Cambrian rocks throughout the southwestern states. Perhaps older geologists will now recall the Geological Society of America presidential address by Charles Schuchert (1923) on the "Sites and Nature of the North American Geosynclines" (FIGURE 1). In this address he describes the Ontarian-Sonorian geosyncline as the oldest known trough of North America. Schuchert's first figure graphically illustrated this geosyncline extending diagonally across North America from northern Sonora through Arizona, Colorado, Wyoming, across to Wisconsin and Michigan, and from there into Ontario.

#### *Review of Geochemical Data*

Aldrich *et al.* (1957) reported the occurrence of 1350 million-year-(m.y.)-old granitic rocks in the western United States. Their data consisted of 10 determinations by both Rb-Sr and K-A on rocks from Arizona, New Mexico, Colorado, and southeastern Wyoming. They also reported younger dates, 1100 m.y., in the Pike's Peak, Colo., region.

A large number of determinations by the K-Ar method for the Pre-Cambrian basement of Colorado have recently been reported by Giffin and Kulp (1960). Their data include dates in the range from 1000 m.y. to 1500 m.y. No evidence was found for a basement older than 1500 m.y. They conclude that their data indicates an event in the period 1300 to 1500 m.y. in which the pre-existing basement was sufficiently heated to have caused the loss of all inherited argon. A less intense orogenic event occurred about 1000 m.y. ago that caused the loss of the inherited argon in the granites and metamorphic rocks of the Pike's Peak area.

Gastil (1960) has tabulated the published dates through January, 1959. A plot of the data indicates a wide area, including dated Pre-Cambrian rocks, 1250 to 1450 m.y. old, centered around the southeastern boundary of Schuchert's Sonoran-Ontarian geosyncline. The area included is much more limited to the northwest than that indicated by Schuchert, who included rocks of considerably older age, and extends further to the southeast to include the Ozark dome and the older Pre-Cambrian of southeastern New Mexico and

Arizona. The data are still far too few, but the trend is interesting and worthy of further consideration.

Little or no published data exists for the Younger Pre-Cambrian of the southwestern states. They have been tentatively correlated with the Beltian sediments by Butler (1933, pp. 205-209), but data is also lacking for the Beltian sediments. According to a personal communication from L. R. Stieff in 1959, uranium ores intruded into the Dripping Springs, Colo., sandstone of the

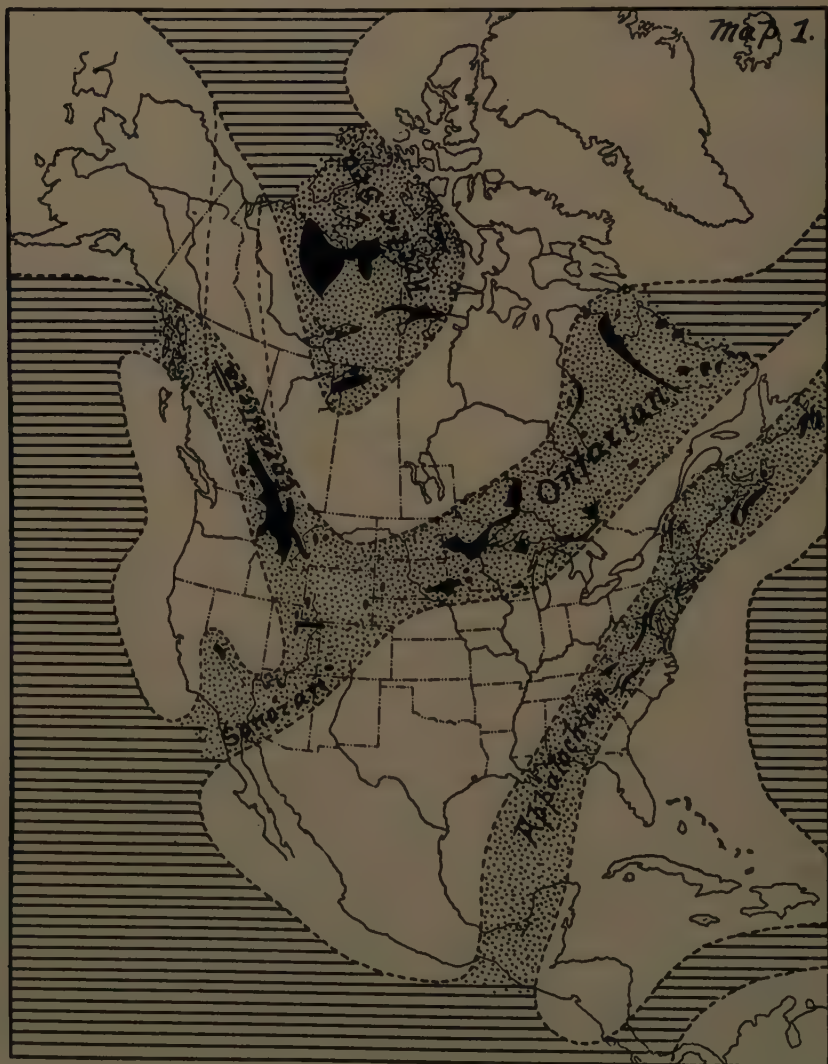


FIGURE 1. Geosynclines (dotted), lands (white), and oceans or mediterraneans (ruled) during late Proterozoic time. Ontarian-Sonoran (Mazatzal geosyncline) from presidential address by Charles Schuchert on "Sites and Nature of the North American Geosynclines." Reproduced by permission from the *Bulletin of the Geological Society of America*, Volume 30.

Apache group have been dated. Stieff states that "the  $\text{Pb}^{207}\text{-Pb}^{206}$  ages lie between 990 and 1100 m.y. An approximate age of 1000 m.y. would probably be correct within  $\pm 100$  m.y." Thus, these ore deposits are approximately contemporaneous with the hypothetical mild metamorphism that resulted in the younger age for the Pike's Peak granite.

*New Rubidium-Strontium Data for Arizona and Sonora*

The new data represents the first results of a cooperative program, engaged in by ourselves, the ultimate goal of which is the obtaining of adequate geochemical data for the Pre-Cambrian rocks of the southwest. The present analyses were carried out at Lamont Geological Observatory, Columbia University, Palisades, N.Y., and at the Department of Geology and Mineralogy, Oxford University, Oxford, England. The details concerning analytical techniques may be found in Gast *et al.* (1958) and Giletti (in preparation) for Lamont and Oxford respectively. The experimental results are given in TABLES 1 and 2.

The statistical precision of the results for the greater than 1000 m.y. ages is  $\pm 3$  per cent s.d. The largest uncertainty lies in the calibration of the isotopic diluent and the correction for common strontium. The standard deviation for Samples 3 and 6 is about  $\pm 30$  per cent because the radiogenic strontium content of Sample 3 is only 0.4 per cent and of Sample 6 only 0.6 per cent of the total strontium content. The Rb-Sr ages given for Mesozoic-Tertiary rocks are only approximations as shown by the large standard errors.

Samples 1 and 2 represent mica separates from a pegmatite and a migmatite, respectively, collected within a few miles of Phantom Ranch at Grand Canyon, Ariz. The Rb-Sr age (1370 m.y.) and K-Ar age (1390 m.y.) for a biotite separate from a gneiss dated by Aldrich *et al.* (1957) are in excellent agreement with Sample 2. The greater age for Sample 1 is probably not experimental but, more likely, it is the result of the different response of the two mica varieties to a complex orogenic event.

The accuracy of the age given for the granite collected 35 miles east of Chloride (Sample 3) is open to question because the sample had a low radiogenic strontium content. Nonetheless, the data tend to confirm an Older Pre-Cambrian age for this granite.

Near Chloride, in northwestern Arizona, a younger granite called the Ithaca Peak granite by Thomas (1949) and the Chloride granite by Dings (1951) intrudes the older Diana granite (Thomas, 1949). Dings assigned the younger granite a Pre-Cambrian(?) age and Thomas suggested it might be Mesozoic(?). The Rb-Sr method gives an age of 1350 m.y. for the Diana granite (Sample 4) and an age of 1210 m.y. for the Chloride granite (Sample 5). Both rocks are Pre-Cambrian. However, the significance of the difference in the ages cannot be determined from the two Rb-Sr dates alone. The ages for the mica separates from these granites are younger than the ages for the two mica separates from rocks of the Grand Canyon Vishnu series. The significance of this difference is also not now known.

The low age obtained for the biotite from the Yavapai schist is uncertain because of the large common strontium correction. Also, the Rb-Sr ratio for



this sample may have been influenced by a basic dike that intrudes the schist in the road-cut from which this sample was obtained. The Yavapai in this area is overlain by Tertiary volcanics.

The age of 1450 m.y. for the Oracle granite biotite separate (Sample 7) falls midway between the limits for the Vishnu series and confirms the existence of an Orogeny of Mazatzal age as far south as Tucson. Previously Banerjee (1957) had considered the Oracle granite in its present form to have been

TABLE 1  
NEW RUBIDIUM-STRONTIUM DATA FOR THE PRE-CAMBRIAN BASEMENT ROCKS  
OF ARIZONA

$$T_{1/2} = 50 \times 10^9 \text{ years}$$

Sample No.	Type of rock, location, and mineral	Rb (ppm)	Sr (normal) (ppm)	Sr <sup>87</sup> */Rb <sup>87</sup>	Age (m.y.)
1	Pegmatite in Vishnu schist, Kaibab Trail, Grand Canyon, Coconino County, muscovite	538	4.31	0.02141	1530
		521	4.69	0.02179	1550
2	Migmatite zone in Vishnu schist, Bright Angel Trail, Coconino County, biotite	630	2.34	0.01943	1390
3	Granite, U.S. Highway 66 near Valentine, Mohave Co., biotite	148	182	0.01810	1300
4	Diana granite, Arizona Chloride Mine, Chloride, Mohave Co., biotite	676	10.5	0.01893	1350
5	Chloride granite, 1/2 mile north of Chloride, Mohave Co., biotite	921	23.3	0.01632	1210
6	Yavapai schist near Prescott on Highway 69, Yavapai Co., biotite	282	84.6	0.006825	~490
7	Oracle granite, near Campo Bonito Mine, Oracle, Pinal Co., biotite	1004	10.13	0.02025	1450

\* Sr<sup>87</sup>, radiogenic strontium.

TABLE 2  
NEW RUBIDIUM-STRONTIUM DATA FOR MESOZOIC-TERTIARY BASEMENT ROCKS  
OF ARIZONA AND SONORA

$$(T_{1/2} = 50 \times 10^9 \text{ years})$$

Sample No.	Type of rock, location and mineral	Rb (ppm)	Sr (normal) (ppm)	Sr <sup>87</sup> */Rb <sup>87</sup>	Age (m.y.)
8	Samaniego granite, about 500 feet from Pirate fault zone, east of Cañada del Oro wash, Pinal Co., biotite	1010	19.5	0.00039	30 ± 30
9	Catalina gneiss, Mount Lemmon Highway at Hitchcock Memorial, Pima Co., biotite-muscovite mixture	458	52.3	0.00221	150 ± 90
10	Adobe Blanco granite, 11 miles south of Sonoita on Puerto Peñasco road, Sonora, muscovite	566	42.3	0.00133	90 ± 60
11	Pegmatite in Altar schist, 2.1 miles east of Altar Village on Highway, Sonora, muscovite	279	56.3	0.00116	80 ± 80

\* Sr<sup>87</sup>, radiogenic strontium.



derived during Pre-Cambrian time by recrystallization and metasomatism of Pinal schist. He interpreted the preferred northeast orientation of biotite and feldspar crystals, schlieren, and inclusions as a deformational feature related to the Mazatzal Revolution (Banerjee, 1957; FIGURE 5).

The Samaniego granite was named by Wallace (1954), who tentatively considered it to be of Pre-Cambrian age. It contains inclusions of Pinal schist and is intruded into the Pinal schist with sharp contacts. It is in fault contact with late Cenozoic sediments on the west and with Pinal schist on the east. Thus, the Samaniego granite is clearly post-Pinal in age, but a more definite estimate cannot be made from the field data. However, the Rb-Sr data, although lacking precision in this time range, definitely demonstrate a Tertiary or at most upper Cretaceous age for at least part of this formation (Sample 8). This could either be the date of intrusion of the granite or of a later metamorphism.

Formerly, the Catalina gneiss, along with all the other regionally metamorphosed rocks of Arizona, was mapped as Pre-Cambrian. More recently Dubois (1959) has suggested a polymetamorphic origin for the gneiss, in its present form, resulting from metamorphism during Older Pre-Cambrian and post-Cretaceous times. The Rb-Sr age of  $150 \pm 90$  m.y. (Sample 9) is not in disagreement with this hypothesis. The authors intend, at a later date, to investigate the biotite and muscovite separately by the K-Ar method.

The Adobe Blanco granite, which is overlapped by Cenozoic alluvium, appears to be Mesozoic in age (Sample 10).

The Altar schist has been tentatively correlated with the Pinal series (Pye and Fries, 1959, p. 11). However, muscovite from a quartz-muscovite pegmatite stringer is apparently Tertiary-Mesozoic in age.

FIGURE 2 illustrates the extent and age of the Older Pre-Cambrian rocks of Mazatzal orogenic age in the Southwest.

### *Conclusions*

From this survey the following tentative conclusions are suggested:

(1) The field data indicate that the southwestern states include the site of a former major geosynclinal trough trending diagonally across the continent in the general direction of Schuchert's (1923) Sonoran-Ontarian geosyncline. The geosynclinal area was the site of extensive volcanism during much of pre-Mazatzal time. During the Mazatzal Revolution, intense folding and faulting was accompanied by the intrusion of granites of batholithic proportions. This resulted in the uplift of a huge mountain range subsequently planed down and unconformably covered by younger sediments.

(2) Geochemical age data indicate that the Mazatzal Revolution occurred during the period extending from 1200 to 1500 m.y. ago. The field data provide no evidence for more than one intense period of Pre-Cambrian metamorphism in Arizona. However, the geochemical data are not inconsistent with a duration of about 200 to 300 m.y. as has been suggested for the average duration of orogenic intervals.

(3) No evidence was found for a pre-existing basement older than 1550 million years. The sediments and volcanics accumulated in the trough prior

to 1500 m.y. before the present. The Older Pre-Cambrian of this region is much younger than the "Archean" of the Canadian shield.

(4) A less intense orogeny resulted in minor faulting and gentle folding of the Younger Pre-Cambrian of Arizona. This event may be quasi-contemporaneous with the origin of the Pike's Peak granite in its present form.

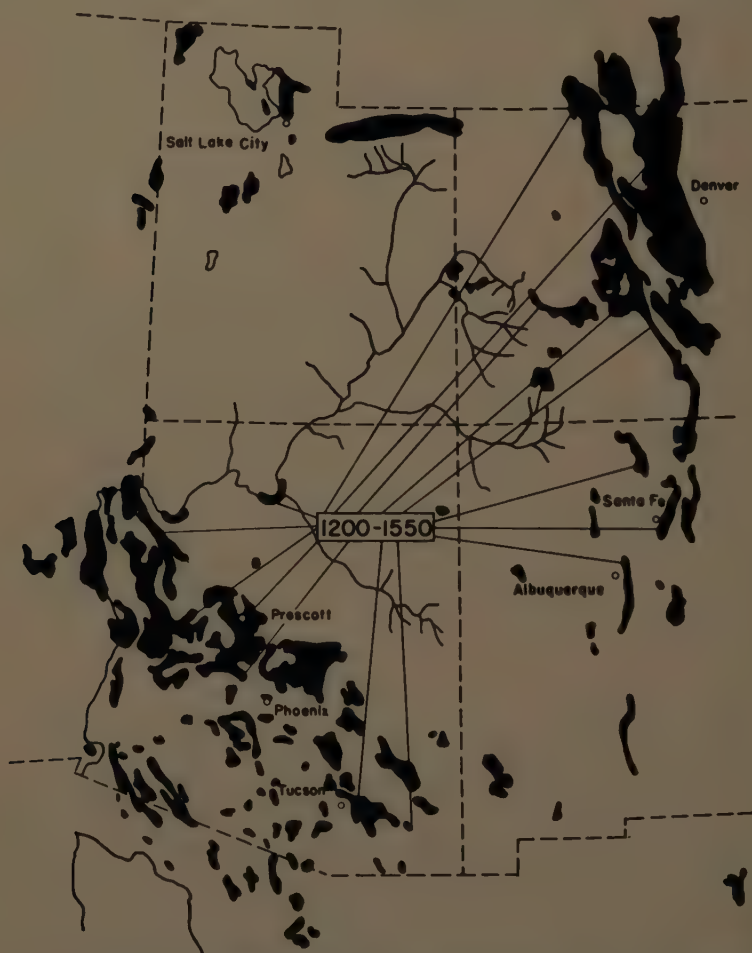


FIGURE 2. Older Pre-Cambrian age of the Colorado Plateau and adjacent areas.

(5) Both geologic field data and geochemical dating indicate that the entire area was relatively stable during all of Paleozoic time and became active again during the Mesozoic-Tertiary Eras.

(6) Large areas of metamorphic and crystalline rock in southern Arizona and Sonora formerly classified as Pre-Cambrian must be reinvestigated. Geochemical dating has demonstrated the occurrence of widespread regional metamorphism in this area during Mesozoic-Tertiary time.

*Acknowledgments*

This work forms part of a program of geological age determinative being carried out by the geochemical section of the University of Arizona Geochronology Laboratories. John Lance and Evans Mayo of the University of Arizona accompanied one of us on several trips to collect samples for dating. It is a pleasure to acknowledge their advice and assistance.

The rubidium-strontium analyses were carried out at Lamont Geological Observatory, Columbia University, Palisades, N.Y., and at the Department of Geology and Mineralogy, Oxford University, Oxford, England, by Giletti.

The authors are grateful to L. R. Wager and E. A. Vincent of Oxford, to J. L. Kulp of Columbia and to F. W. Galbraith and T. L. Smiley of the University of Arizona for encouraging this cooperative endeavour.

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### *Discussion of the Paper*

J. L. KULP (*Columbia University, New York, N.Y.*): Could these low ages, particularly in the gneiss, simply reflect mild heating due to Tertiary intrusives rather than actual metamorphism in the Tertiary? From S. R. Hart's work and other factors reported elsewhere in this monograph, it seems that you do not need very much of a temperature rise to lower K-Ar biotite ages and you did have a lot of Tertiary activity in the area.

DAMON: The Samaniago granite is intrusive into the Pinal series with sharp contacts and it appears to be genuine intrusive granite. It could, however, be remobilized Oracle granite and this has been suggested.

In the case of the Catalinas, of course, much more work has to be done before we can know what is going on there. Most probably this is a case of polymetamorphism, older Pre-Cambrian rocks metamorphosed in the Pre-Cambrian remetamorphosed in the Mesozoic-Tertiary.

As far as the Adobe Blanco granite in Mexico is concerned, this is again an equigranular granite. It seems that this is a case of a fairly large granitic block emplaced in the Tertiary. I do not think there is any doubt about the fact that we have included many Tertiary-Mesozoic rocks in the Pre-Cambrian of Arizona and post-Paleozoic extensive regional metamorphism occurred during this time.

GILETTI: It should be noted that several of the very young dates were muscovites rather than biotites. Further, we wish to point out that we believe the original metamorphism was probably Pre-Cambrian, but so far we have not obtained mica ages older than Tertiary-Mesozoic.

DAMON: The 490 m.y. date on the biotite from the Yavapai series near Prescott is anomalous. It had a high common strontium content, but we can not explain the date on this basis. However, in restudying the road cut we found a basic dike in the vicinity and the Yavapai in this area had been covered by Tertiary volcanics.

There is no evidence for metamorphism in the Paleozoic in Arizona, and I prefer temporarily to leave this for further investigation. Most probably it is Pre-Cambrian and subsequently altered.

L. T. SILVER (*California Institute of Technology, Pasadena, Calif.*): I want to support Damon's comments about the probable existence of this younger material in Arizona. Anyone who is familiar with the geology—and I have spent about ten years in there—will know that there are many, many aspects of tectonics including major deformation and emplacement of large plutons at



about this time. Everything in the environment is perfectly compatible with the kind of picture Damon has presented.

I shall also make a point or two about the existence of specific episodes in these older rocks that Damon has been discussing. I think it is quite clear that the major older granites in Arizona and, as far as that goes, in Colorado too, include rocks as old as 1700 m.y.

The Johnny Lyon granodiorite is the last major episode of a complicated Pre-Cambrian interval in southeastern Arizona; whether you use the interpretation that G. R. Tilton uses or the episodic interpretation I suggested, Tilton and I agree that this rock has zircons in it that are essentially 1700 m.y. old.

In addition, quite some time ago, Tilton, in working over the Quartz Creek, Colorado rocks, found he had among zircon fractions from two different samples: first, a group of ages that were somewhat discordant, running from approximately 925 to 1540 m.y., and then a second zircon on which he did only a Pb-Pb age, but a very good one, of 1700 m.y. Also, if the combination of the discordance plus this lead age is taken, they still give a 1700 m.y. interpretation.

For that accumulation of age data where we have as yet what we might call uncorroborated individual numbers for individual rock masses, it is quite possible that a great many of the numbers are intermediate numbers in response to some of the difficult problems that Wetherill proposed and that we have seen emphasized again and again in the data in different articles in this monograph.

Thus I shall say quite probably there was an event somewhere around 1700 m.y. ago in the southwest. I think there are real events that are younger. Just where they fall in the younger spectrum is slightly difficult to say at this stage of the game. One last comment: the organization and the integrity of both the structure and the lithology of the older Pre-Cambrian in the southwest has been commented on by a number of workers—among them, myself—and in this particular case I shall say that there is a very strong series of arguments for integrating an orogenic history.

I think that even without the radioactive ages it is possible to make impressive arguments in terms of structural unity and the basic lithologic character of the rocks that are involved, and this, I think, is one of the important points that can be made about Pre-Cambrian in this area.

M. KAY (*Columbia University, New York, N.Y.*): We are getting some of the same controversies that were going on 10 or 15 years ago between Wilson and others with regard to the classification of rocks. They are going to be solved by these methods I believe.



# ABSOLUTE AGE OF PRE-CAMBRIAN ROCKS IN WYOMING AND MONTANA\*

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A number of absolute-age determinations from the Cordilleran region of the western United States (Aldrich *et al.*, 1956; Aldrich *et al.*, 1958; Giffin and Kulp, 1960) established that a widespread rock-forming event occurred about 1350 million years (m.y.) ago. These measurements were made on rocks in the region from central Arizona to southernmost Wyoming. Gast *et al.* (1958) demonstrated that a regional metamorphism affected rocks in the Beartooth Range (Montana to Wyoming) 2700 m.y. ago and that this event probably extended to the Bighorn Range. The purpose of the present preliminary study was to establish the extent of the 2700-m.y.-old rocks and to ascertain whether any rock-forming events between the ages 1350 m.y. and 2700 m.y. might be found.

The rock samples used in this study were collected by us in the summer of 1957. The experimental procedures employed in this study were essentially similar to those previously described (Gast *et al.*, 1958). Isotope-dilution analyses employed enriched  $\text{Sr}^{86}$  and  $\text{Rb}^{87}$  tracers. Most of the isotope-ratio measurements were made on the mass spectrometer described by Gast *et al.* (1958). Some measurements were made on a Metropolitan Vickers MS-5 mass spectrometer in the Department of Geology at Oxford University, Oxford, England.

The results are shown in TABLE 1. Part A lists the very old ages of central and western Wyoming. Parts B, C, and D list the younger ages from the areas surrounding this old region. Geographic locations of the samples are shown in FIGURE 1.

The determinations in TABLE 1, Part A, and in FIGURE 1 show that rocks older than 2400 m.y. probably cover a substantial part of the state of Wyoming. With the exception of Samples 2 and 3, the ages in TABLE 1, Part A, are fairly consistent. However the variation seen among the different samples studied here, from 2370 m.y. to 2720 m.y., is considerably greater than that found by Gast *et al.* (1958). A number of samples, particularly biotites, give ages significantly younger than those reported for the Beartooth region.

The results from the Teton region are of particular interest. Three samples from Death Canyon, collected within 200 feet of each other, have been studied. Coexisting muscovite and microcline from a pegmatite intruding a biotite gneiss gave ages of 2660 m.y. and 1990 m.y. respectively. Biotite from the surrounding gneiss yields an age of 1360 m.y. Finally, pegmatitic biotite

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collected 8 miles east of Jackson, Wyoming (about 17 miles southeast of Death Canyon) gives an age of 1760 m.y. It seems highly probable that the variable age found for these samples is the result of thermal or ground water alteration.

TABLE 1  
RUBIDIUM-STRONTIUM AGE MEASUREMENTS FROM THE NORTHERN ROCKY MOUNTAIN REGION\*

Locality	Mineral	Age (m.y.)
A. Northern and central Wyoming		
1. Pegmatite cutting Brighteyed gneiss, Death Canyon, Teton Range	Muscovite	2660
	Microcline	1990
2. Brighteyed gneiss, Teton Range	Biotite	1360
3. Pegmatite east of Jackson, Wyo.	Biotite	1760
4. Pegmatite, Peat Lake, northern Wind River Range	Muscovite	2540
5. Quartz monzonite, southern Wind River Range	Biotite	2370
6. Pegmatite, Wind River Canyon	Muscovite	2720
7. Pegmatite, north of Bonneville, Wyo.	Microcline	2640
8. Banded gneiss, Powder River Pass, Big-horn Range	Biotite	2550
9. Biotite gneiss, Casper Mountain, Casper, Wyo.	Biotite	2450
B. Southeastern Wyoming		
10. Biotite gneiss, western Medicine Bow Range	Biotite	1720
11. Pegmatite (Platt Prospect)	Biotite	1660
12. Banded gneiss, eastern Medicine Bow Range	Biotite	1520
13. Sherman granite, Vedauvoo Camp ground	Biotite	1420
C. Southwestern Montana		
14. Dillon granite gneiss, Tendoy Range	Biotite	1560
	Total Rock	1550
15. Pony gneiss, Dell, Mont.	Biotite I	1630
	Biotite II	1570
16. Garnet, muscovite biotite schist, east of Dillon, Mont.	Muscovite	1810
	Biotite I	1620
	Biotite II	1660
17. Cherry Creek gneiss, Ramshorn Creek, Virginia City, Mont.	Biotite	1620
18. Pegmatite, in Cherry Creek gneiss, Alder, Mont.	Muscovite	1700
	Microcline	1640
D. Utah and South Dakota		
19. Pegmatite, Bountiful Peak, Salt Lake City, Utah	Muscovite	1580
20. Bob Ingersoll Mine, Keystone, S.D.	Lepidolite	1620

\*  $\text{Rb}^{87}$  half life =  $50 \times 10^9$  years.

tion. The closely associated biotite, muscovite, and feldspar of the Death Canyon locality furnish a good example of the different susceptibilities that these minerals have toward such alteration. The discordance between different minerals found in this region suggests that the area may be in a boundary zone between rocks of different ages. Similar situations showing in particular

the susceptibility of biotite to loss of radiogenic daughters have been found in a number of other studies (for example, Tilton *et al.*, 1958; Kulp *et al.*, 1959; and papers appearing elsewhere in this monograph).

Because biotite is so susceptible to loss of radiogenic daughters, the interpretation of age determinations made on a single sample of biotite cannot be made without some ambiguity. In TABLE 1, Part A for example, it is difficult to say whether biotites such as Samples 5 and 9 really are younger than some of the muscovite samples or have suffered some alteration. In any case, it

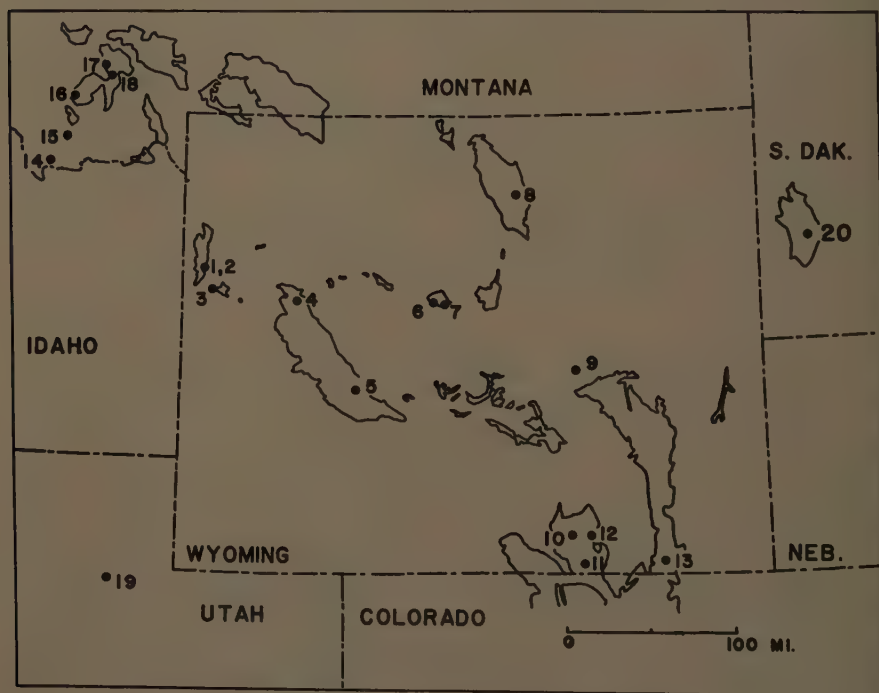


FIGURE 1. Pre-Cambrian outcrop and sample locations (see text).

seems safe to conclude that rocks older than 2300 m.y. occur in the Teton, Wind River, and Bighorn Ranges, and that these may possibly extend as far south as Casper, Wyo.

The exposure of Pre-Cambrian rocks in the regions surrounding the old area described above is rather limited in most directions. The best areas for finding a possible transition into younger rocks are southeastern Wyoming and southwestern Montana. A number of determinations have been made on rocks from these areas.

Results from the Medicine Bow and Front Ranges are listed in TABLE 1, Part B. A single measurement on biotite from a typical sample of Sherman granite gives an age of 1420 m.y. This is in agreement with K-Ar and Rb-Sr ages of 1380 and 1410 m.y. respectively reported by Aldrich *et al.* (1958) for a

sample of Sherman granite from a different locality. It is clearly lower than the 1540-m.y. K-Ar age reported by Giffin and Kulp (1960) for granite from a similar locality.

The Pre-Cambrian rocks of the Medicine Bow Range have been described by Blackwelder (1926). They consist of a northeast-trending belt of meta-sediments flanked by gneissic rocks. Two samples from the western flank of the range have been analyzed. Biotite from a biotite gneiss in the north-western part of the range gave an age of 1760 m.y. A pegmatitic biotite approximately 20 miles southeast of this sample gave an age of 1660 m.y. A sample of banded gneiss from the eastern flank of the range gave an age of 1520 m.y. The metamorphic terrain represented by these samples was presumably intruded by the Sherman Granite. The ages found here suggest that this terrain is significantly older than the Sherman Granite, assuming that the correct age for this intrusion is 1400 m.y. Whether the biotites from the gneissic rocks represent the real age of these rocks and/or whether they all represent a second metamorphic event superimposed on a much older rock cannot be established from the present data. In either case there appears to be some evidence for a metamorphism (between the 1350-m.y.-old rock-forming event in the southern Rocky Mountains and the much older event seen to the northwest), probably during the time 1600 to 1750 m.y. ago.

Results from southwestern Montana are given in TABLE 1, Part C. This area has been described by Tansley *et al.* (1933) and Scholten *et al.* (1955), who divided the Pre-Cambrian into three groups, the Pony gneiss, the Cherry Creek gneiss, and the Dillon granite. The temporal relations of these rocks are still a matter of dispute (Scholten, 1955; Reid, 1955). All the biotite ages from these rocks fall in the range 1560 to 1660 m.y., regardless of the type of rock from which they come. The muscovite and microcline ages are somewhat higher (up to 1800 m.y.). A whole-rock analysis on a split taken from the Dillon granite rock powder gave an age of 1550 m.y. The agreement of the whole rock and the biotite age suggests that the Dillon granite cannot be very much older than 1600 m.y. The possibility that the Dillon is actually much older cannot be ruled out until further study can show whether such granites behave as closed systems. The muscovite ages from the pegmatite in the Cherry Creek gneiss (Sample 18) and the muscovite schist east of Dillon are an indication of a possible older event. The ages from the Dillon granite and the consistency of the biotite ages seem to indicate a rock-forming event in this area approximately 1600 m.y. years ago.

TABLE 1, Part D, gives two additional measurements. Lepidolite from the Bob Ingersoll Mine gives a Rb-Sr age of 1620 m.y., in good agreement with the more extensive work of Wetherill *et al.* (1956). A single muscovite sample from Bountiful Peak, Utah, gives an age of 1580 m.y.

In conclusion, the present survey indicates: (1) that 2300 to 2700-m.-y.-old rocks are of major importance among the Pre-Cambrian rocks of Wyoming, covering large areas in western and central Wyoming; and (2) that there is a substantial amount of evidence for a metamorphic event in the age range 1550 to 1700 m.y. in several regions bordering on the very ancient rocks mentioned above.

*Acknowledgments*

Most of the work reported here was done at the Geochemical Laboratory of The Lamont Geological Observatory, Columbia University, Palisades, N.Y. We are grateful for the assistance and advice of R. S. Houston, Department of Geology, University of Wyoming, Cheyenne, Wyo., who aided in the collection of the Medicine Bow samples. The Oxford measurements were supported by the Department of Scientific and Industrial Research and the Overseas Geological Surveys, London, England.

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*Discussion of the Paper*

GILETTI: I wish to present two minor notes to the paper. First, the figures quoted by P. W. Gast should be rounded off to the nearest 10 million years. Second, there seems to be a metamorphic event at 1600 m.y. Whether we can say that there are two events, that is at 1600 m.y. and at 1800 m.y., the important thing is that something is seen at 1600 m.y. that does not agree with the 1350-m.y. range that P. E. Damon and I have observed in the southwest.



## PERIODS OF OROGENY IN THE WESTERN CORDILLERA

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The explanation of the history and method of formation of large granitic bodies in a given mountain chain is a formidable problem, and the relation between large volume events in various parts of the world is still uncertain. These problems encompass the data of relative heights, tremendous interrelated volumes, varying temperature and phase properties, solid state (or other state) ion mobilities and solubilities, relative areas, cross-section information, crystal properties, field relations, and of course, geologic time. I am sure that this naive listing is incomplete. The hope is that some day we shall be able to say that the Chilliwack and Snoqualmie Batholiths were emplaced 18 million years (m.y.) ago at a certain depth, in known volume, and at known temperature and pressure because of some unique chain of geologic mechanics that started on its unalterable path when the earth was a molten ball.

Geochronology gives the geologist two types of data. If an age of a rock determined by different methods and on different minerals is concordant, the geologist is given an absolute date that other information must check against (Aldrich *et al.*, 1958). If ages by different methods are discordant or if ages of different minerals by the same method are discordant, the geologist is given clues to geologic events that may be of even greater value. In this spirit I present some age determinations of some Western Cordillera batholiths. These ages were determined solely by the K-Ar method.

According to previous work (Curtis *et al.*, 1958) the granite of the Sierra Nevada Range in California was formed between 80 and 95 m.y. ago. An older emplacement with ages ranging from 134 to 143 m.y. was found immediately adjacent to the Sierra Nevada granites.

Moving north to the Western Cordillera of Canada, Robert Folinsbee of the University of Alberta has collected a large number of intrusive granites from batholiths of the Western Cordillera. Definite intrusive events occurred 350 m.y. ago in the Ice River Intrusive at Field, British Columbia, and about 160 to 185 m.y. ago in the Guichon Batholith and the Topley Granite. No intrusive rocks matching the 130 to 140 m.y. old granites of California have been found in Canada. The 80-100-million-year age of the Sierra Nevada Mountains is matched by the age of the extensive Coast Range of British Columbia and by the age of several intrusive bodies to the east of the Coast Range (Gottfried *et al.*, 1959; Baadsgaard *et al.*, 1961).

The area in British Columbia between the Coast Range and the Rocky Mountains exhibits great geologic complexity (FIGURE 1). It may not be surprising, then, that several intrusive bodies have been found that are younger than the 100 million years of the Coast Range. Several ages between 50 to 60 m.y. have been reported (Baadsgaard *et al.*, 1961). Two Cordilleran granites, Cascade and Hell's Gate, have recently yielded ages of about 35 m.y. One of

these, Cascade, is a gneiss and some argon may have been lost as a result of a recent event.

The previous samples have had their age and geologic description discussed elsewhere. I shall present the evidence concerning two Miocene granites located in the Western Cordillera. On the evidence of excellent field work (Smith and Calkins, 1906; Grant, 1941; and Waters, 1955), Buddington (1959) considers the Snoqualmie Batholith of Washington to be a Miocene emplace-

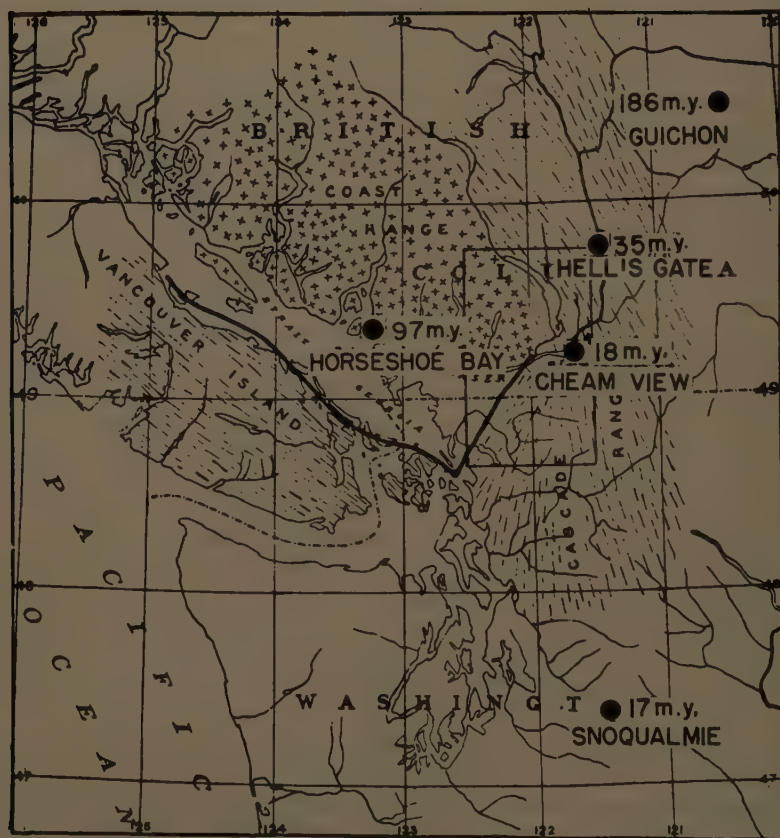


FIGURE 1. Potassium-argon dates: coast and cascade range.

ment into the epizone (near surface region) of the crust. He believes that in the Cascade Range of Washington a possibly extensive batholith (4000 square miles; Knopf, 1955) is being uncovered by erosion. This age classification is verified by the K-Ar age of 17 m.y. for a sample from the Snoqualmie Batholith. The sample was obtained from a road cut east of Seattle,  $47^{\circ} 23' \text{ N. } 121^{\circ} 28' \text{ W.}$

The age of the Chilliwack Batholith of Washington and British Columbia has been uncertain since it was first mapped at the request of Daly (1912) at the beginning of the century. Until recently the entire area had not been mapped,

and what was considered to be one batholith we now consider to be two different bodies. As mapped by Misch (1952) and Crickmay (1930), the Chilliwack Batholith is about 5 to 10 miles wide from east to west and about 35 miles long from north to south. The material collected by Folinsbee came from the Chilliwack Batholith where it is cut by the Fraser River. One sample came from the Wahleach Lake Powerhouse,  $49^{\circ} 14.5' \text{ N. } 121^{\circ} 41' \text{ W.}$  on the Fraser, while the other came from the Valley Granite Products Quarry one mile away,  $49^{\circ} 15.5' \text{ N. } 121^{\circ} 41' \text{ W.}$  Both samples are from a stock in the granodiorite and both samples are miarolitic, indicating emplacement at shallow depth. Both samples yield a K-Ar age of 18 m.y. on the biotite from the rock. The identity of the age with that of the Snoqualmie raises the possibility that the Chilliwack Batholith dated by us is part of the same intrusion being uncovered in the Cascade Range in Washington.

Let us look at the field reports. Daly, working north of the 49th parallel in 1912, says: "The date of the intrusion of the main (Chilliwack) batholith can be fixed within certain limits. . . . It follows (from the relation to fossiliferous Carboniferous slates) that the granodiorite is of post-Carboniferous date. At no point does it show evidence of crushing or of pronounced straining; . . . there can be little doubt as to the relatively late date of intrusion. In field habit as in many essential microscopic details, this granodiorite is like that of the post-Cretaceous Castle Peak stock. There are, thus, some grounds for the belief that the Chilliwack granodiorite was, like the granodiorite at Snoqualmie Pass to the southward, intruded at a date as recent as the Miocene." Crickmay, writing in 1930 and interpreting the evidence, says: "One such (Cenozoic) body, almost large enough to be called a batholith, lies across Harrison River valley just below the efflux of the lake, and extends to the southeast passing north of Agassiz, crossing the Fraser at Cheam View, and continuing into the mountains beyond Wahleach Lake." In conclusion he decides, ". . . formations and structures are continuous from the Cascade Mountains of Washington to the 'Cascades' of British Columbia. In other words these two groups of mountains though separated by the Fraser Valley are structurally one. They were formed as a continuous chain early in the Cenozoic." Misch (1952) believes that the Chilliwack granodiorite is the result of granitization of the Skagit gneiss. This granitized material is then to have been mobilized and to have intruded metamorphic rocks on the Western contact: "It is thus indicated that at least part of the Chilliwack granodiorite and quartz diorite has been active after the Early Cretaceous."

Finally, Foster (1960) agrees with the young age of the Snoqualmie granodiorite but adds that Larsen *et al.* (1952) obtain a date of 63 m.y. for the granite from Snoqualmie. While they admit that the run was poor and that they consider the date to be much too high, a rerun on a sample by Howard Jaffe and communicated to Foster by Larsen also gave a zircon age of 60 m.y. This was considered to be a good run. The second specimen was collected from White river, north of Goat Island Mountain near Mt. Rainier, Wash.

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### *Discussion of the Paper*

J. L. KULP (*Columbia University, New York, N.Y.*): We have dated three samples of biotite from the Skagit gneiss several miles from the contact with the Chilliwack granite by K-Ar obtaining 43, 44, and 48 m.y. Since the original metamorphism was pre-Tertiary, these probably represent transitional zone values. A sample of biotite from the Chilliwack gave 34 m.y., which I understand G. H. Curtis also ran and from which he obtained about the same result. Thus all of the Chilliwack is not part of the Miocene granitic intrusions dated by Lipson and Robert Folinsbee. Furthermore, if the dates on the Chilliwack are also transitional, some of what is called Chilliwack may be also pre-Tertiary. If this is true, Peter Misch's hypothesis could still have validity.

S. C. ROBINSON (*Canadian Geological Survey, Ottawa, Canada*): The Geological Survey of Canada is carrying out a detailed study of granites in southeastern British Columbia that includes the Nelson batholith. This "batholith" is a complex body that is intruded by Tertiary rocks. It includes the Valhalla granites where J. E. Reesor of the Geological Survey has demonstrated that granitic gneisses overlie quartzites. In these rocks three biotites yielded ages ranging from 11 to 16 m.y., yet biotite from Nelson granite at a quarry near Nelson gives an age of 86 m.y.

It seems probable that a series of discrete and clearly-defined intrusive granites and granodiorites, further to the east, including the Adamant, Bugaboo, and White Creek bodies are generally younger than the main Nelson granites, yet they have often been loosely correlated with the Nelson batholith. It is apparent that it would be unwise to attempt to establish one age for a group of rocks as complex as those correlated with the Nelson batholith.

Recent examination of the Ice River syenites by Reesor indicates that they are intrusive into the lower Paleozoic rocks of the Rocky Mountains. Biotites from these syenites gave K-Ar ages of 330 and 340 m.y.

DAMON: May I ask Lipson if these were dates on mica separates or the whole rock.



J. LIPSON (*University of Alberta, Edmonton, Canada*): They were on biotite from these rocks.

L. T. SILVER (*California Institute of Technology, Pasadena, Calif.*): I think the people who are working in the older rock groups, in the Pre-Cambrian rocks, probably should take a good look at the information that this paper has provided and keep this in mind. We get to the problem back about anywhere from 1 to  $2\frac{1}{2}$  billion and we start worrying about dispersion effects and we want to know whether as an example, it is possible to have intrusions that are 2.4 versus 2.6 billion years apart in the same region and, of course, we must worry about the analytical dispersion.

However, on the other hand, here we can see a region in which there appears to be good evidence for intrusion at perhaps 20- or 30-m.-y. intervals from more than 100 m.y. ago to the present, and it is quite clear that it is possible to find, in fact, in a given area that kind of a dispersion in time. I do not think this represents anything unique in geological history. I think perhaps a little more uniformity might be expected.

DAMON: Something I had meant to say before in interpreting these dates from 1200 to, perhaps, 1600 m.y. is this: the single orogeny which Eldred Wilson and other geologists call for in Arizona and in the southwestern states actually may not be a single orogeny. The dates thus far are consistent with a hypothesis that would involve a range of, perhaps, 250 million years such as you have in the Appalachians going from Taconic through the Appalachian event. I do not think that you can absolutely dispense with this possibility yet.

L. T. ALDRICH (*Carnegie Institution of Washington, Washington, D.C.*): This is not a question, it is just additional data that I am surprised H. Faul has not given. It should be pointed out now that it appears possible to obtain micas that can be dated in this age range by the Rb-Sr method also. The rock that E. Jaeger dated was a notable example of something that is 18 m.y. old; about 30 per cent of the strontium-87 is radiogenic.

I have just finished dating one that was about 25 m.y. old in the Little Cottonwood stock near Salt Lake City, and it is about 4 per cent radiogenic; nevertheless, with sufficient care one can at least get in this ball park providing you are patient enough with your mineral separation.

H. FAUL (*United States Geological Survey, Washington, D.C.*): Rocks can be found that are 18 million years old and can be dated by Rb-Sr. Emily Jaeger has proved that. However, we should not expect to do that on any rock. The rocks dated were unusually clean micas. All apatite was outside the mica crystals, and there were few flaws and no other inclusions. Such mica is extremely rare.

G. R. TILTON (*Carnegie Institution of Washington, Washington, D.C.*): In the Washington-Baltimore area, the Kensington gneiss biotite on which ages were done by, I believe, Wetherill, the common strontium in this mica was so low that, if its age had been 18 m.y., Wetherill would have obtained ages of comparable accuracy with those of the Alpine samples.

G. W. WETHERILL (*Carnegie Institution of Washington, Washington, D.C.*): I am not sure about this concerning the Kensington gneiss. We looked over our data right after the run that Jaeger did and, as I recall, there were several samples (I hesitate to give the statistics on them) having small but sufficient amounts of common strontium to make accurate dating possible on them.



## Part V. The Age of the Basement Rocks of the World: Eurasia

### THE BASEMENT ROCKS OF SCOTLAND AND IRELAND

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The complex relations among the basement rocks of the British Isles have been studied since at least 1819.<sup>1-3</sup> Three major groups have been established: the Lewisian, the Moine, and the Dalradian. The well-defined Pre-Cambrian basement is the Lewisian Complex, exposed in northwest Scotland west of the Caledonian Moine Thrust. To the southeast the Moine Series occupies the ground between the Moine Thrust and the Great Glen Fault and extends into the Central Highlands. The Dalradian lies approximately between the Moines and the Midland Valley of Scotland.

The Lewisian has been divided into two parts,<sup>4</sup> the earlier Scourian and the later Laxfordian, on the basis of structural and petrological evidence. Feldspars from both Lewisian episodes were taken for K-Ar analysis by Holmes *et al.*<sup>5</sup> who reported a mean age of  $1090 \pm 70$  million years (m.y.). It has been pointed out already that the Holmes *et al.* data are minimum values.<sup>7</sup> Smales *et al.*<sup>6</sup> analyzed three Lewisian feldspars by Rb-Sr, obtaining ages of  $1555 \pm 60$ ,  $1790 \pm 350$ , and  $235 \pm 90$  m.y. The two Pre-Cambrian dates agree with the dates to follow, but no explanation is known for the 235 m.y. date, which was given by an albite. The only other isotopic age determinations on Lewisian materials are three lead isotope analyses of galenas<sup>8</sup> that give model ages ranging from 650 to 800 m.y. (although they may be anomalous).

The Moine rocks of Scotland have been assigned to various Pre-Cambrian episodes. The Moine metamorphism has been correlated with the Laxfordian<sup>9</sup> and with the Caledonian,<sup>10</sup> while the original sediments have been correlated with the Torridonian sandstone.<sup>11</sup> The latter overlies the Lewisian with profound unconformity and is, in turn, overlain unconformably by the Cambrian.

The remaining major unit of the Scottish metamorphics, the Dalradian, is a series of metamorphosed sediments that have been correlated in part<sup>12</sup> with the Cambrian and are generally considered to be Eocambrian-Cambrian. The Connemara Schist of western Ireland is thought to be equivalent to the Dalradian.

The major problem in establishing the ages of the Moine and Dalradian rocks arises from the superposition of a Caledonian metamorphism on the previous history. This, coupled with extensive thrusting and multiple folding, has isolated these formations and thus prevented useful correlation. It is generally thought that the Dalradian sediments are younger than the Moine; both are overlain unconformably by Devonian sediments. The Aberdeen granite intrudes the Dalradian and gives a Rb-Sr age of  $367 \pm 50$  m.y.<sup>6</sup>

The new ages reported here have been obtained by the Rb-Sr method and

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include representatives of all the metamorphics discussed above. K-Ar analyses will be made in the near future. The Rb-Sr analyses were performed using stable-isotope dilution techniques.  $\text{Sr}^{86}$  and  $\text{Rb}^{87}$  tracers were added to the purified mineral and the whole dissolved in HF and  $\text{HClO}_4$ . Rubidium was coprecipitated with potassium as the perchlorate from the resulting solution and was not purified further. Strontium was isolated by using ion exchange. The mass spectrometer was a Metropolitan-Vickers MS-5 solid source machine with an electron multiplier. The samples of rubidium and strontium were usually mounted on separate single-tantalum filaments. The ratios obtained were corrected (by the usual factor of the square root of the atomic mass ratio) for discrimination by the electron multiplier. All dates quoted employ a  $\text{Rb}^{87}$  half life of  $4.7 \times 10^{10}$  years<sup>13</sup> and, where other workers' dates are quoted, the ages have been recalculated using this half life.

A few results from this laboratory have appeared previously<sup>7</sup> and are also listed here. These have all been lowered by 6 per cent to conform with the  $4.7 \times 10^{10}$  year half life. Further, a few have been modified by 1 to 2 per cent owing to further calibrations on one set of tracers.

Data from the type locality of the earlier, Scourian, phase of the Lewisian are shown in TABLE 1 A. It is inferred that the biotite suffered more than the K-feldspar during the later Laxfordian metamorphism. As the feldspar age is also probably a minimum date, the Scourian metamorphism may be considerably older than 2500 m.y. It is suggested, however, that the most likely age is in the range 2500 to 2800 m.y.

The type locality for the Laxfordian is north of Loch Laxford, although these rocks have been tentatively correlated with Lewisian rocks to the south near Loch Maree and Loch Torridon.<sup>4</sup> Other samples come from South Harris. Three types of specimens of Laxfordian gneiss and one of a contemporaneous pegmatite are shown in TABLE 1 B. These average 1440 m.y. The feldspar is noteworthy both because it is a different mineral and because of its very high common strontium content. The feldspar date supports the use of the normal common strontium isotopic abundances in correcting for original strontium in the minerals of this area.

Three micas from South Harris are also shown in TABLE 1 C. These represent two possible metamorphic episodes (R. Dearnley, personal communication), but all agree and give an average of 1510 m.y. They are considered contemporaneous with the mainland Laxfordian and suggest that the Laxfordian metamorphism included most of Harris and, by analogy, most of Lewis.

Other samples shown in TABLE 1 D giving Laxfordian ages include the metasediments northeast of Loch Maree. A small area presumed to be Scourian<sup>4</sup> near Loch Torridon also gives a Laxfordian age, but it is within one-half mile of Laxfordian-type rocks and the biotite is assumed to have been reconstituted. One of the structural transition zones from Scourian to Laxfordian, the Foindle zone, also gives a Laxfordian date. The spread in the Laxfordian ages is not solely an analytical effect and may reflect proximity to Caledonian events.

Turning now to the Moine rocks in north and central Scotland, several samples were analyzed in order to date the Moine metamorphism. Four widely separated samples give ages that average 420 m.y. (TABLE 2). The remaining

sample is a muscovite from a concordant pegmatite and gives 740 m.y. The two Knydart specimens were within 100 yards of each other. It is inferred that the pattern of ages here again gives evidence that book muscovite is more

TABLE 1  
RUBIDIUM-STRONTIUM AGES OF THE LEWISIAN COMPLEX,  
NORTHWEST SCOTLAND

Description	Mineral	Rb (ppm)	SrN (ppm)	Sr <sup>87</sup> (ppm)	Age (m.y.)*
(A) Scourian phase Pegmatite, Scourie	Potassium feldspar	759	151	8.17	2520 ± 50
		752	160	7.84	2450 ± 40
		746	146	7.67	2420 ± 40
Pegmatite, Scourie More	Biotite	1474	26.8	12.7	2030 ± 45
		1476	27.0	12.5	2000 ± 65
(B) Laxfordian phase Gneiss, Durness	Biotite	669	17.3	4.01	1420 ± 30
		628	16.2	3.90	1470 ± 55
Gneiss, Rhiconich Bridge	Biotite	535	12.8	3.47	1530 ± 35
		561	12.8	3.54	1490 ± 30
Pegmatite, 2.3 mi. N. of Laxford Bridge	Biotite	500	29.8	2.98	1410 ± 30
		459	41.8	2.81	1450 ± 40
	Feldspar	323	536	2.01	1470 ± 200
Gneiss, near Laxford Bridge	Biotite	566	29.0	3.24	1350 ± 30
		566	28.2	3.04	1280 ± 30
		552	32.3	3.30	1410 ± 40
(C) Harris, Outer Hebrides Pegmatite, Chiapaval	Muscovite	3314	1.81	22.0	1570 ± 40
		3251	2.50	22.1	1610 ± 35
Gneiss, Northton	Biotite	327	25.3	1.99	1440 ± 40
		318	27.2	2.02	1550 ± 40
Pegmatite, Sletteval	Biotite	1321	2.33	8.55	1530 ± 30
		1392	2.99	8.55	1450 ± 30
(D) Various localities Schist, L. Marce Ross-shire	Muscovite	291	33.5	1.85	1510 ± 40
		294	33.9	1.92	1540 ± 45
Gneiss, L. Torridon Ross-shire	Biotite	401	21.9	2.20	1300 ± 30
Gneiss, Foindle zone Sutherlandshire	Biotite	540	90.3	3.11	1360 ± 90
		526	108	3.25	1460 ± 60
		566	106	3.38	1420 ± 65

\* Constant:  $t_{1/2} = 4.7 \times 10^{10}$  years.

stable to later metamorphism than biotite. It is suggested that this relict age of 740 m.y. is the minimum age of the pegmatite formation and thus of the Moine sedimentation.

If the pegmatite formed while the Moine sediments were being metamorphosed, this earlier metamorphism could be Laxfordian or some undated

orogeny between 1500 m.y. and 740 m.y. ago. The latter suggestion would still permit the Moine sediments to be equivalent to the Torridonian.

The last group of formations studied included the Dalradian near Pitlochry in Scotland and its probable equivalent, the Connemara Schist in western Ireland.

TABLE 2  
RUBIDIUM-STRONTIUM AGES OF MOINE ROCKS, SCOTLAND

Description	Mineral	Rb (ppm)	SrN (ppm)	Sr <sup>87</sup> * (ppm)	Age (m.y.)
Schist, Bettyhill, Sutherland-shire	Biotite	518	7.37	0.92	425 ± 9
Schist, Braemore, Ross-shire	Biotite	544	9.74	0.995	435 ± 10
Granite, Carn Chuinneag, Ross-shire	Microcline	486	3.42	0.850	415 ± 9
		486	2.32	.847	415 ± 9
Schist, Knoydart, Inverness-shire	Biotite	292	9.23	0.512	415 ± 11
		326	8.75	0.571	420 ± 12
Pegmatite, Knoydart Inverness-shire	Muscovite	991	21.3	3.06	740 ± 15
		987	20.2	3.07	740 ± 25

\* Constant:  $t_{1/2} = 4.7 \times 10^{10}$  years.

TABLE 3  
RUBIDIUM-STRONTIUM AGES OF THE CONNEMARA SCHIST, EIRE, AND THE DALRADIAN OF SCOTLAND

Description	Mineral	Rb (ppm)	SrN (ppm)	Sr <sup>87</sup> * (ppm)	Age (m.y.)
Schist, Clifden, County Galway, Eire	Muscovite	356	27.6	0.733	490 ± 22
		359	24.9	0.748	495 ± 22
	Biotite	616	20.7	1.18	460 ± 12
Pegmatite in schist, Clifden, County Galway, Eire	Muscovite	356	9.88	0.693	465 ± 13
		356	8.67	0.690	460 ± 11
Dalradian, Bonskeid, Perthshire, Scotland	Biotite	359	7.46	0.711	470 ± 11
		368	6.71	0.692	455 ± 10

\* Constant:  $t_{1/2} = 4.7 \times 10^{10}$  years.

These presumed Eocambrian-Cambrian rocks average 470 m.y. (TABLE 3). Unconformities have been found<sup>14</sup> both above and below the Arenig formation (Lower Ordovician). This metamorphism may therefore be late Cambrian or middle Ordovician. Definitive field evidence is lacking.

Work in all these areas is continuing; meanwhile these results constitute a progress report rather than a summary of the study. The conclusions drawn thus far may be summarized as follows. The two Lewisian episodes are widely separated in time, with the Scourian at least 2500 m.y. old and the Laxfordian about 1500 m.y. old. The Torridonian sediments are less than

1500 m.y. old. The Moines, at least in Knoydart, are probably Pre-Cambrian sediments, but were metamorphosed about 420 m.y. ago. The Connemara schist and one Dalradian sample indicate a metamorphism at about 470 m.y. ago.

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# SOME POTASSIUM-ARGON AGES ON ROCKS FROM THE NORWEGIAN BASEMENT\*

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This paper is a preliminary report of a continuing study of the age of the Norwegian basement by the various isotopic methods. The first phase has been a reconnaissance survey of the K-Ar isotopic ages in mica from representative rock units. The mineral separations were done in Oslo, Norway. The analyses of the potassium and the radiogenic argon were made by standard isotope dilution techniques at the Lamont Geological Observatory, Palisades, N.Y. The isotopic ratios from which the isotopic ages are calculated are believed to be accurate to 3 per cent.

In the most general aspect the surface geology of south and central Norway may be divided into areas of high-grade gneisses and schists shown in FIGURE 1 by the white areas, the latest Cryptozoic (Pre-Cambrian) to Cambro-Silurian sedimentary rocks that have experienced Caledonian folding shown by the diagonally lined area, and the Oslo depression (crosshatched) that contains essentially unmetamorphosed Cambrian and Permian. Within the zone of high-grade gneisses and schists is a variety of igneous and metamorphic rocks showing clear evidence of multiple metamorphic events. In the far north the rocks are all metamorphosed or remetamorphosed by the Caledonian orogeny.

The results are summarized in TABLE 1, and the dates are plotted on FIGURE 1 with the exception of those in the province of Nordland. In attempting to interpret these data it must be realized that isotopic ages on mica are equal to or less than the last time of crystallization. Even slight heating can cause loss of argon from fine-grained biotite such as is commonly encountered in gneisses and schists, and temperatures well below those required for metamorphism may cause argon loss from even book muscovite. K-Ar ages without supporting information can therefore be regarded only as minimum ages, although similarity in isotopic K-Ar ages over a large area involving micas of different type and size suggests that a real event is being dated.

Initially it is seen (FIGURE 1) that there are no K-Ar ages on these mica samples as old as those of the Lewisian of northwest Scotland, that is Scourian 2500 m.y. and Laxfordian 1450 m.y. (Giletti, 1960). The original basement in all or part of Norway could have been this old but, if such were the case, later metamorphic events have heated the rocks sufficiently so that the radiogenic argon accumulated in the original micas was lost. The oldest isotopic ages obtained by micas in this study were from southernmost Norway (Langsev and Aust-Agder, 1345 m.y.).

The youngest metamorphic event in Norway appears to have been the

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Caledonian (~400 to 420 m.y. ago). Along the west coast in the central part of the country the basement rocks underlying the lightly metamorphosed but folded Cambro-Silurian sequence are exposed. These rocks show the super-imposed Caledonian structures. It is clear from the K-Ar isotopic dates on



FIGURE 1. Location of potassium-argon dates on mica samples from the basement rocks of Norway.

the mica from Hordaland and Romsdal (425, 405, and 390 m.y.) that the accumulated radiogenic argon was lost when these micas were heated and/or recrystallized in the Caledonian orogeny. At Bleikvassli in southern Nordland a similar age is obtained (that is, 395 m.y.). These ages average only

TABLE 1  
POTASSIUM-ARGON AGES ON MICA FROM ROCKS OF NORWAY

Locality	Sample	Radio- genic Ar <sup>40</sup> cc/gm. × 10 <sup>4</sup>	K %	Isotopic age (m.y.)*
Southern Norway				
Langsev, Aust-Agder	Biotite in arendalite	5.22	6.71	1345
Lörenskog, Akershus	Biotite in gneiss	4.51	7.55	1105
Hisøy, Aust-Agder	Biotite in gneiss	4.43	7.39	1105
Bamle, Telemark	Biotite in apatite-vein	3.65	6.30	1080
Modum, Buskerud	Muscovite in pegmatite	4.67	8.30	1055
Hisøy, Aust-Agder	Biotite in arendalite	3.44	6.49	1010
N. Tinnsjø, Telemark	Biotite in granite	1.40	2.81	965
Hedal Church, Buskerud	Biotite in granite	2.15	4.38	950
Assevvann, Aust-Agder	Biotite in gneiss	3.46	7.13	940
Tromsund, Aust-Agder	Biotite in pegmatite	3.48	7.21	935
NNE Flaten, Aust-Agder	Biotite in mica schist	2.00	4.20	925
Tarjeisberg, Telemark	Book biotite in pegmatite	3.07	6.57	915
Krødsherrad, Buskerud	Sericite in pegmatite	3.82	8.39	895
Flaten, Aust-Agder	Biotite in gneiss	3.20	7.28	870
Herefoss, Aust-Agder	Biotite in granite	2.67	6.14	860
Iveland, Vest-Agder	Muscovite in pegmatite	3.72	8.61	860
Tvedestrand, Aust-Agder	Biotite in granite	2.52	4.51	850
Fenik, Aust-Agder	Biotite in granite	2.37	5.56	850
Iddefjord, Østfold	Biotite in granite	2.33	5.63	839
Romteland, Vest-Agder	Biotite in Forsundite	1.89	4.58	825
So. Sundslø, Aust-Agder	Biotite in granite	2.06	5.09	815
Holla, Telemark	Biotite in Kimberleyite	1.90	6.96	585
West Coast Caledonian				
Alversund, Hordaland	Muscovite in pegmatite	1.61	8.52	425
Geiranger, Romsdal	Biotite in gneiss			405
Dalsnibba, Romsdal	Biotite in gneiss			385
Northern Caledonian				
Bleikvassli, Nordland	Muscovite in pyrite ore	1.43	8.20	395
Vesterålen, Nordland	Biotite in grey gneiss	1.52	7.93	430
	Biotite in mica schist	1.67	8.23	450
	Biotite in augen gneiss	2.01	7.52	575
	Book biotite in pegmatite	1.435	7.62	423

\* Constants:  $\lambda_B = 4.72 \times 10^{-10} \text{ yr.}^{-1}$  and  $\lambda_K = 0.584 \times 10^{-10} \text{ yr.}^{-1}$ .

slightly older than the actual times ( $\sim 390$  m.y.) of intrusion of the postkinematic Caledonian granites of Great Britain (Kulp *et al.*, 1960).

In a limited area in the islands of the northwestern coast of Nordland micas from a series of rocks (TABLE 1) show K-Ar isotopic ages ranging from 430 to 575 m.y. These may be most simply interpreted as representing various degrees of loss of radiogenic argon of rocks older than 575 m.y. by the Caledonian event.

In southern Norway the Caledonian orogeny appears to have been either absent or to have produced only minor effects. The isotopic ages range from

815 to 1345 m.y. with possible clusters near 1100 and 900 m.y. The zone of gneisses and schists passes to the southeast into Sweden where K-Ar dates by the Soviet workers suggest thermal activity 1000 to 1100 m.y. ago.

The presence of an 1100-m.-y. event in Norway is supported by several measurements. On cleveite from a pegmatite at Holt, Aust-Agder, Nier (1939) obtained concordant U-Pb and Th-Pb ages at 1090 m.y. Any significant alteration of such a mineral causes strong discordance in these ages, hence this appears to be a primary age. In addition, the Modum sample (1055 m.y.) is book muscovite from a pegmatite. Several other samples of biotite from the gneisses in southern Norway give ages in this range, for example, Lörenskog (1105 m.y.), Bamle (1080 m.y.), and Hisøy (1105 m.y.), although in these cases the possibility cannot be ruled out that these merely represent transitional stages of older rocks that have lost part of their radiogenic argon subsequent to 1100 m.y. ago.

Clear evidence for a later metamorphic event in southern Norway at about 910 m.y. is the concordant U-Pb age pattern on uraninite and euxenite from Romteland, Vest-Agder (Kulp and Eckelmann, 1957). Rb-Sr age on feldspar from a pegmatite at Tordal gave 890 m.y. (Catanzaro and Gast, 1960). Other pegmatite minerals not inconsistent with an event at about this time are Tromsund (935 m.y.), Tarjeisberg (915 m.y.), Krødsherrad (895 m.y.), and Iveland (860 m.y.), since the experimental error in this age range is about  $\pm 30$  m.y. Actually about 12 samples lie within two standard deviations of 905 m.y. The three samples of biotite in granite or gneiss that fall below this range are Iddefjord (830 m.y.), Romteland (825 m.y.), and South Sundsli (815 m.y.). Whether these have lost argon due to their inherently poor structure or a later thermal event such as may have been associated with the Caledonian cannot be ascertained with the data available. This question will be resolved by additional measurements on other mineral phases. Despite these few low values, it appears clear that the Caledonian thermal effect was minor in southern and southeastern Norway.

Biotite from a dike rock in the Fen area (Holla, Telemark) gave an intermediate age of 585 m.y. in good agreement with that reported by Faul *et al.* (1959) on biotite from a carbonatite rock (565 m.y.). In view of the absence of Caledonian effects in this area and the crosscutting character of these rocks, the results suggest an early Cambrian igneous intrusion.

Since the Telemark gneiss of southern Norway appears to be more recent than the basement metamorphic complex and the  $910 \pm$  m.y. pegmatite event intrudes the Telemark type igneous rocks, the primary age of the basement would appear to be much older.

It is interesting to note that the time of these two Pre-Cambrian metamorphic events (910 and 1090 m.y.) in Norway lies between the minimum age obtained by Giletti (1960, p. 1793) for the primary metamorphism of the Moine in Central Scotland (740 m.y.) and the time of widespread Laxfordian metamorphic sequence in the Lewisian of northwest Scotland (1450 m.y.) that probably underlies the Moine sequence. It is tempting, therefore, to suggest a correlation of this tectonic activity in Norway at 900 to 1100 m.y. ago with the metamorphism of the Moine rocks in the classic area of Scotland.

The basement rocks of Norway have clearly undergone multiple metamor-



phism. This phenomenon is emerging as commonplace in the history of continents.

### *Acknowledgment*

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### *Discussion of the Papers*

LAMBERT: In view of the general interest in this question of the retention of a sort of "fossil" age by these micas, I shall just comment on the geological background of the Knoydart sample.

There is some fairly direct evidence about the temperature of the metamorphism.

The pegmatite is shown on the sketch map (FIGURE 1). In the initial metamorphism, which affected the whole area, the temperature was probably about 650° C., an approximate temperature plus or minus 100° C. I think, for the formation of that pegmatite.

Subsequently, according to my own researches, there was a second metamorphism in part of the area of the sketch map. In the region in the southwest part there occurred complete recrystallization showing a temperature of about 450° ± 100° C.

The region affected by the second metamorphism is separated from the unaffected area of the first metamorphism by a transition zone about one-half mile wide beyond which there is no microscopic recrystallization except for minor disturbances of miscellaneous minerals such as garnet. The horizontal distance from the pegmatite to the transition zone at the present time is about 2½ miles.

G. J. WASSERBURG (*California Institute of Technology, Pasadena, Calif.*): May I ask how these temperatures were obtained?

LAMBERT: The actual figures are based on "muscovite-paragonite" backed by a general consideration of the mineralogy. Analyses of muscovite coexisting with albite were plotted on Yoder's subsolidus curve for muscovite-paragonite to give the figures mentioned. The absence of paragonite from these rocks suggests that the figures are a minimum, but the curve itself may be erroneous and is likely to err in the direction of too high a temperature. The calcium content of the rocks and the pressure at the time of metamorphism



may also affect the curve. In general, the pegmatite is situated within the kyanite-zone of regional metamorphism, quite close (approximately 1 mile) to the first development of sillimanite and the first appearance of rocks of "migmatite" type in which partial melting of the "granite" fraction has occurred. This presumably develops close to the ternary minimum melting temperature of the system quartz-albite-K feldspar (approximately 700° C. at a high  $P_{H_2O}$ ).

GILETTI: Concerning the suggestion made by J. L. Kulp about correlating an approximately 900-m.y. event with, for example, the Lewisian or Moine: there does not seem to be any serious problem here even if it is assumed that the Moine equals the Torridonian, because there is still sufficient time for the Torridonian to be deposited and subsequently metamorphosed at about 900

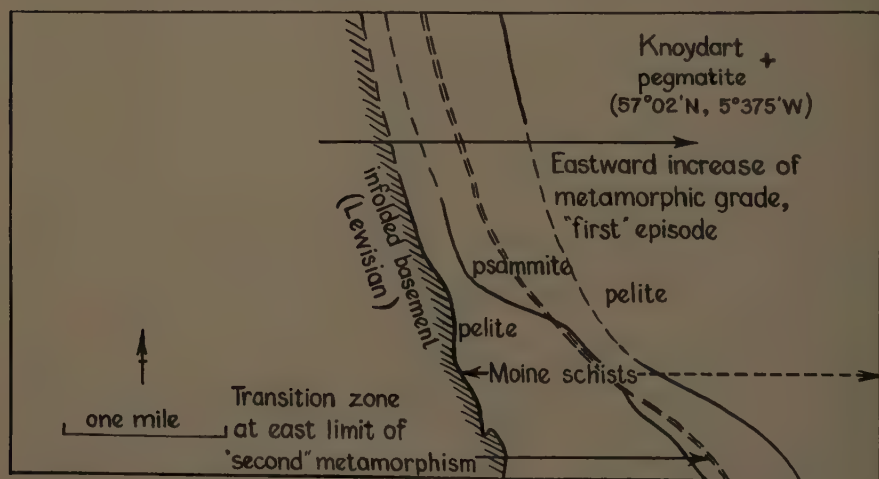


FIGURE 1. Geological sketch map of part of the Morar Structure, western Scotland, showing approximate eastern limit of the "second" (retrogressive) metamorphism.

m.y. ago. After all, there is from 1500 to 900 m.y. for Torridonian deposition, burial, and metamorphism.

Another point: these data show that the correlation of the Laxfordian in northwest Scotland with the Arendal orogeny in Norway (both at 1000 m.y.) by Holmes *et al.* in 1955 are incorrect. A feldspar from Arendal has been dated by Webster (Smales *et al.*, 1958) at about 1035 m.y., using the new decay constant consistent with the K-Ar data shown by Kulp. The Laxfordian in contrast clearly occurred about 1450 m.y. ago.

G. W. WETHERILL (*Carnegie Institution of Washington, Washington, D.C.*): A. A. Smales and R. K. Webster reported at the Geneva Conference a figure of 1750 m.y. for rubidium-strontium on the feldspar. What does this mean in terms of the work reported here?

GILETTI: Is this a reference to the Laxfordian?

WETHERILL: It is rather to your work on the Lewisian in general.

GILETTI: The data are as follows. Smales and Webster give  $1555 \pm 60$

m.y. and  $1790 \pm 350$  m.y. for rocks that are both Lewisian, but the dates agree analytically with the time of the Laxfordian metamorphism at about 1450 m.y. They also have a  $235 \pm 90$  on an albite moonstone, but I have no idea what that means and neither do they at the moment. That is the total of the Lewisian dates.

WETHERILL: Is the 740-m.y. figure going to be checked by some other method? If this is really 740 m.y., it is important because no such age has been found anywhere except in confusion resulting from two events neither of which was at 740 m.y.

GILETTI: We are most interested in the sample that gave the 740-m.y. age. In fact, in addition to this particular locality, we expect to be going back in the next few weeks to do further collecting in the general area. We hope to do K-Ar measurements among other things in the near future. This paper is primarily a progress report on work still being done.

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# ISOTOPIC COMPOSITION OF FINNISH GALENAS\*

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## *Introduction*

The Pre-Cambrian rocks of Finland appear to have experienced a number of orogenic events (at possibly 2800, 2100, and 1800 million years), each preceded by at least one major period of geosynclinal deposition. The last major event was the intrusion of the Rapakivi rocks at about 1650 m.y. ago (Kouvo, 1958; Simonen, 1960; Tilton, in press; Wetherill *et al.*, in press). This rough outline of the metamorphic history was made possible by isotopic age measurements based on the radioactive decay schemes  $U^{238}\text{-Pb}^{206}$ ,  $U^{235}\text{-Pb}^{207}$ ,  $Rb^{87}\text{-Sr}^{87}$ , and  $K^{40}\text{-Ar}^{40}$  on suitable minerals.

In order to add further information to this complex problem it was decided to examine the isotopic composition of the lead and the sulfur in galena samples from veins, disseminations, and ore deposits in each of the metamorphic provinces. The massive ore bodies are particularly definitive in this regard due to the difficulty of contamination or alteration of the original isotopic composition. If the lead in a galena of a metamorphic province has had a simple history, its isotopic composition will indicate the time of mineral formation. By a simple history it is meant that the lead in the galena either has been derived directly from the mantle or, as appears more common, it has come from average crustal lead in geosynclinal sediments that have spent only a relatively short life in the geosyncline prior to ore formation. If the sulfur is either isotopically very heavy or very light, it is clear evidence that the sulfur in the sulfide was derived from an original sedimentary environment (Ault and Kulp, 1960).

The specific objectives of this investigation were: (1) to determine the uniformity and, if possible, the age of the galenas associated with the Svecofennian rocks; (2) to search for possible differences in the history of the Karelian and Svecofennian rocks prior to the 1800-m.y. orogeny; (3) to look for ancient lead in the Saamian basement complex on which the Karelian sediments were deposited; and (4) to attempt to learn more about the mechanism by which the ore bodies have been formed.

## *Experimental Techniques*

The galena was carefully purified either by hand selection under the microscope or by the use of heavy liquid, magnetic, and flotation techniques. For the lead isotope analysis the sample was prepared and examined mass spectrometrically by the techniques described by Miller and Kulp (in press). The reproducibility of the  $Pb^{206}/Pb^{204}$ ,  $Pb^{207}/Pb^{204}$ , and  $Pb^{208}/Pb^{204}$  ratios was at

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least  $\pm 0.5$  per cent. Significant systematic discrimination was absent, as confirmed by analysis of a gravimetrically prepared isotopic mixture and inter-comparison of surface emission and lead-tetramethyl gas techniques. The sulfur determinations have been reported earlier by Ault and Kulp (1960) and were reproducible to  $\pm 0.05$  per cent. Their measurements were related to Cañon Diablo troilite sulfur as the primary standard.

### *Geological Setting*

At least six Pre-Cambrian metamorphic or plutonic episodes appear to be represented in Fennoscandia. They have been approximately dated by analyses of radioactive minerals at several laboratories (Kouvo, 1958; Gerling and Polkanov, 1958; Wetherill *et al.*, in press). A large number of K-Ar determinations on separated micas from all rock provinces have been reported. The Karelian and Svecofennian rocks gave the same mica ages on numerous specimens and also similar ages on a few selected zircon samples from the so-called late and synkinematic granites and granodiorites. Zircon, feldspar, and mica ages by the U-Pb, Rb-Sr, and K-Ar methods on the ancient basement showed it to be much older (probably about 2800 m.y.) but that it was widely affected by later metamorphic events (Wetherill *et al.*, in press).

These samples are arranged in the order of increasing age:

(1) The recent isotopic ages (Gerling and Polkanov, 1958; Kulp and Neumann, elsewhere in this monograph) have confirmed the chemical ages by F. E. Wickman (personal communication) for radioactive minerals from the early recognized Gothic belt in southern Norway and Sweden at 900 to 1100 m.y.

(2) The Rapakivi and some other anorogenic potash granites were intruded at about 1650 m.y.

(3) The radioactive minerals from plutonic rocks intruding the Svecofennian and Karelian belts as well as the enclosing schists, gneisses, and migmatites have shown zircon ages of about 1800 m.y.

(4) The isotopic ages collected from northern Lapland and the White Sea region have been found to be 1900 to 2100 m.y.

(5) Ages of 2700 to 2800 m.y. have become increasingly evident in several parts of Fennoscandia, especially characterizing the basement rocks beneath the Karelian sediments.

(6) The oldest minerals thus far known have been found from Kola peninsula, U.S.S.R. where mica of 3400 m.y. has been reported by Gerling and Polkanov (1958) and confirmed by measurements at the Lamont Geochemical Laboratory.

Gerling and Polkanov (1958) have suggested the old names Belomorian (Mare Albian, White Sea) and Saamian for the formations giving dates of 2100 and 2800 m.y. respectively and the name Katarchean for the very ancient rocks in Kola.

The age groups of 1650, 1800, and 2800 m.y. are now defined in a reasonably satisfactory way in Finland (Kouvo, 1958; Wetherill *et al.*, in press). The existence of the 1900 to 2100 event is suggested by a 1900-m.y.  $\text{Pb}^{207}\text{-Pb}^{206}$  age on zircon from the granulite area in Finnish Lapland.

The main features of the Finnish Pre-Cambrian are shown by the map in FIGURE 1.

One of the most striking features is the boundary zone between the Karelian rocks and the ancient basement that stretches north-northwest from Lake



FIGURE 1. Locations of the samples investigated: 1a, pre-Karelian granite gneiss basement; 1b, granulite arch; 2, Svecofennian schist belt; 3, Karelian schist belt; 4, Rapakivi rocks. Reproduced by permission of *Bulletin Commerce geologie Finlande* (Simonen, 1960).



Ladoga. In the easternmost region the ancient gneissose zone is present. This basement rock can be found also in some mantled domes (Eskola, 1949) in the Karelian province. The isotopic ages on zircons (Tilton, in press; Wetherill *et al.*, in press) for this pre-Karelian basement area have indicated 2700 to 2800 m.y. as the probable time of initial metamorphism. The Karelian metasedimentary column lying upon this Saamian basement complex represents a foreland sequence of deposition: basal conglomerate, arkosite, huge beds of quartzite, mica schist, and minor constituents such as carbonate rocks (dolomites), black schists, pillow lavas, and banded iron ores. This lithologic association is especially well developed in the southern part of the ancient mountain chain where the sequence is intruded by the Kitee granite of 1800-m.y. age.

In southwestern Finland a well-studied section of geosynclinal deposits, 7000 to 8500 m. thick, has been described by Simonen (1953). These metasedimentary rocks are intruded by plutonic rocks of various tectonic types yielding zircon ages of about 1800 m.y.

The alleged differences between these two schist belts—Karelides in eastern and northern Finland and Svecofennides in southwestern Finland—are as follows:

(1) These ancient mountain chains have been considered to be two separate orogenic belts, the Karelian rocks being younger.

(2) The strike of the arcuate zones of the Karelian mountain chain is north-northwest in the southern parts but east to west in the north. The strike of the Svecofennian range comes in at west-southwest from central Sweden but also forms a huge arc turning from the east to west to a north to south direction.

(3) Karelides are characterized by vast quartzites lying upon the Saamian gneissose basement and conglomerates, including pebbles from these basement rocks. Svecofennides are almost lacking in quartzites.

(4) The ultramafic rocks, generally serpentinites characterizing the Karelides, are easily followed for hundreds of kilometers. Very few ophiolite-like bodies can be detected in the Svecofennian mountain chain.

(5) Dolomitic carbonate rocks prevail in the Karelian province while only calcites are found in the Svecofennian area.

(6) The intrusive rocks penetrating both of these mountain chains are dated at about 1800 m.y. whereas the Saamian basement area in eastern part of Finland shows an age as high as 2800 m.y. and in northern Lapland at least 1900 m.y. (Wetherill *et al.*, in press).

As to the nomenclature, it has long appeared a difficult problem to decide whether the sediments in the Savo schist belt (west of the typical Karelian schist belt), as well as the schists in southeastern corner of Finland, belong to the Svecofennian or to the Karelian formation.

During recent years it has become evident that the stratigraphic methods used with so much success in the study of younger mountain chains, have a wide application also in the study of the deeply eroded ancient mountain chains. Mikkola (1953 and 1959) was the first to suggest that the Svecofennian orogenic belt could be explained as the geosynclinal facies (Simonen, 1953) of the Karelian foreland or platform facies.

As regards the two main orogenic belts, the isotopic ages indicate that both areas were metamorphosed at 1800 m.y. ago, but these ages do not preclude a prior and possibly different history for these belts. According to Eskola (in press) the similar isotopic ages in the Karelian and Svecofennian rocks might be explained "... as proving an enormous regeneration of rocks in the Archean: in the Svecofennian areas the regeneration has gone to an end, in the old kraton of Karelia it has not been complete. The regeneration has befallen those areas which belonged to the mobile belts, i.e., to orogenic zones, orogeny being a geochemical as well as a geotectonic process."

The new data discussed below bear on this interesting problem and may assist in its solution. It seems likely, however, that much additional information, including further fieldwork, will be required before there can be a reasonable understanding of these relationships.

### *Results*

The distribution of the samples studied is shown in FIGURE 1. The geographic and petrographic description of these samples is given in the APPENDIX.

The majority of samples are from Finland. Seven of them are from the former Finnish area now belonging to the Union of Soviet Socialist Republics.

Special attention has been paid to the three schist zones, that is, the Svecofennian schist belt in southern and western Finland, the Karelian schist belt in eastern and northern Finland, and the Savo schist belt west of the Karelian belt. Seventeen of the samples originate from fairly large ore bodies.

The lead isotopic-abundance data for the samples grouped by geologic provinces are given in TABLE 1. Also, the calculated time of deposition is given assuming: (1) the lead has had a normal history, that is, it has come from a crustal environment with an average Pb/U ratio; (2) the age of the earth is  $4.6 \times 10^9$  years; and (3) the primeval isotopic composition of lead is that determined by Patterson on meteoritic troilite (Patterson, 1956). The ages calculated from the model have an absolute uncertainty of about  $\pm 100$  m.y. The uncertainty in the age of a given sample from the analytical error is about  $\pm 40$  m.y. (standard deviation).

The sulfur isotopic data (Ault and Kulp, 1959 and 1960; H. G. Thode, personal communication; Kouvo, 1958) are given in FIGURE 4. Average crustal sulfur has a sulfur isotopic composition of  $S^{32}/S^{34} = 22.12$ .

The trace-element content of most of the Svecofennian samples has been reported earlier by Vaasjoki (1956) and Vaasjoki and Kouvo (1959).

### *Discussion*

All of the lead-isotopic data are plotted on the isochron diagram (FIGURE 2). The most striking feature is the consistency of the model ages of all of the Svecofennian samples taken over a distance of 300 to 400 km. These samples lie on the 1800-m.y. isochron within the analytical error. This probably means that the time of ore formation occurred at about 1800 m.y. ago immediately following the metamorphic event dated as  $1810 \pm 25$  m.y. by U-Pb isotopic ages on zircons.

TABLE 1  
ISOTOPIC ABUNDANCES OF LEAD FROM SOME FINNISH GALENAS

No.	Source	Pb <sup>206</sup> / Pb <sup>204</sup>	Pb <sup>207</sup> / Pb <sup>204</sup>	Pb <sup>208</sup> / Pb <sup>204</sup>	Model age (m.y.)
<i>A. Rapakivi</i>					
1.	Sottunga Sulfide vein	22.30	16.42	40.54	Modern
2.	Säkkijärvi Sulfide vein	19.50	16.09	39.87	Modern
3.	Luumäki Sulfide vein	19.33	16.31	39.61	Modern
4.	Säkkijärvi Sulfide vein	19.15	15.80	39.13	Modern
<i>B. Petsamo</i>					
5.	Suolavuono Quartz-sulfide vein	17.54	15.59	37.34	630
6.	Peuravuono Quartz-sulfide vein	17.28	15.56	37.24	775
<i>C. Svecofennides</i>					
7.	Hopeavuori Sulfide mineralization	16.13	15.60	36.42	1670
8.	Aijala Sulfide deposit	15.95	15.64	36.24	1820
9.	Korsnäs Galena in carbonatite (economic ore)	15.95	15.57	36.26	1770
10.	Pernaja Sulfide vein	15.85	15.51	36.00	1780
11.	Attu Small sulfide mineralization	15.82	15.47	35.89	1780
12.	Orijärvi Sulfide deposit	15.80	15.46	35.88	1770
13.	Pakila Small mineralization	15.73	15.36	35.30	1730
14.	Ylöjärvi Copper ore deposit	15.53	15.28	35.28	1810
<i>D. Savo schist zone</i>					
15.	Viitasaari Sulfide mineralization	15.64	15.32	35.10	1760
16.	Pihtipudas Mineralized zone	15.42	15.09	34.71	1710
17.	Säviä Quartz vein associated with sulfide mineralization	15.54	15.20	34.78	1730
<i>E. Karelian vein type</i>					
18.	Keihäsjoki Native lead in soil (from veins like Panjavaara)	15.92	15.70	36.06	1900
19.	Kiiminki Veinlike quartz patch in phyllite	15.92	15.57	35.38	1800
20.	Panjavaara Carbonate vein	15.74	15.45	35.98	1810
21.	Kuurna Quartz vein	15.72	15.43	35.54	1800
22.	Vallitunsaaari Quartz-calcite vein	15.30	15.45	35.09	2140
23.	Ahmoavaara Patches of carbonate in serpentinite	15.39	15.20	34.99	1830
24.	Nunnanlahti Veins in amphibole skarn rock	13.64	14.81	34.14	2900
<i>F. Karelian ore bodies and sulfide disseminations</i>					
25a.	Pyhäsalmi Massive sulfide ore	15.23	15.29	35.23	2050
25b.	Pyhäsalmi Massive sulfide ore	15.12	15.15	34.89	2010
26a.	Vihanti Massive sulfide ore	15.08	15.24	35.31	2070
26b.	Vihanti Massive sulfide ore	15.20	15.29	35.54	2125
27.	Pattijoki Sulfides in skarn rock	15.02	15.11	34.91	2050
28.	Petrovaara Small sulfide accumulation	14.79	15.00	34.34	2090
29a.	Lupikko Pitkäranta ore field	14.84	14.92	34.66	2040
29b.	Herberz I Pitkäranta ore field	14.73	14.88	34.51	2080
29c.	Beck, Hopun-vaara Pitkäranta ore field	14.79	15.01	34.72	2160
30a.	Outokumpu Sulfide ore	14.90	15.23	35.21	2270
		14.84	15.21	35.29	2270
30b.	Outokumpu Sulfide ore	14.77	15.13	34.85	2290
<i>G. Ancient Saamian Basement</i>					
31.	Huhus Galena mineralization	14.62	15.02	34.55	2300
32.	Varpaisjärvi Galena in aplitic granite	14.14	14.93	34.31	2530

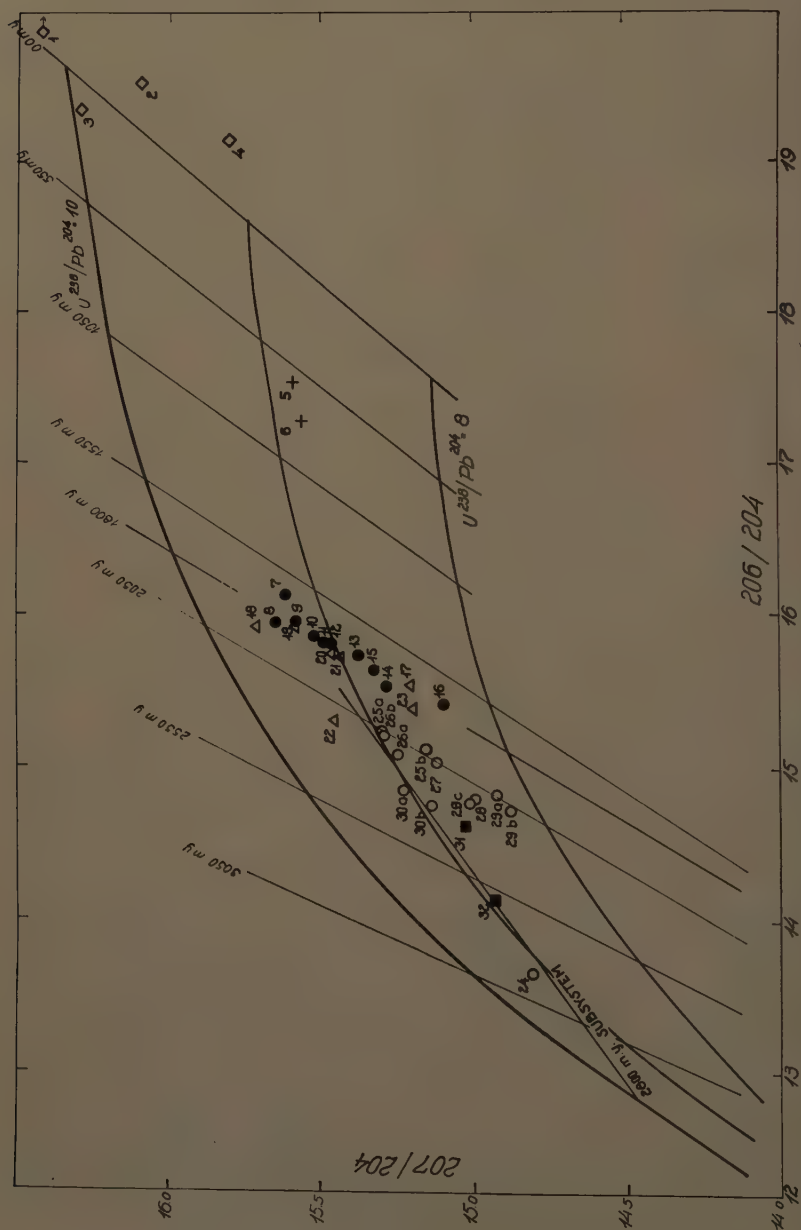


FIGURE 2. Isochron plot of  $Pb^{207}/Pb^{204}$  and  $Pb^{208}/Pb^{204}$  ratios: Rapakivi veins; + Petsamo veins; ● Svecofennides and Savo schist belt; ○ Karelides; △ small veins and patches in the Karelian rocks; ■ Saamian basement complex.

The galena samples from the Karelian rocks represent a great variety of mineralogical occurrence from tiny quartz-carbonate veins to the massive ore bodies such as Pyhäsalmi, Vihanti, and Outokumpu.

Most of the small veinlets in the Karelian belt and the three samples from the Savo schist belt carry galena that yields a model age of 1800 m.y. within experimental error. As regards small veinlets and patches of sulfides, they may have been derived from local rocks with average U/Pb ratio at the time of the 1800-m.y. event. Two other small occurrences in Karelian rocks show model ages older than the 1800-m.y. event, that is, Vallitunsaari and Nun-

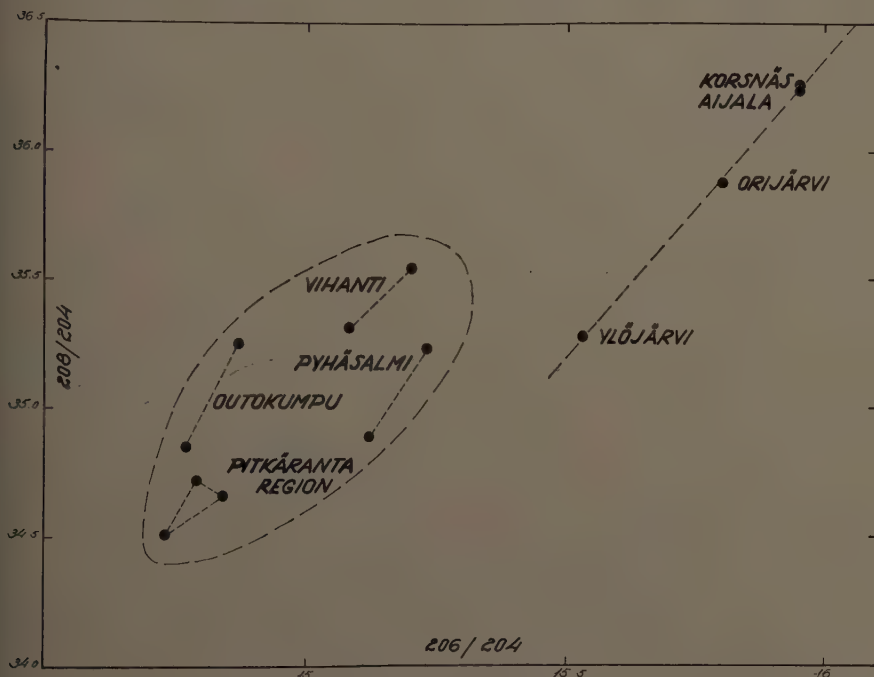


FIGURE 3. Plot showing isotope ratios  $Pb^{208}/Pb^{204}$  and  $Pb^{206}/Pb^{204}$  for lead samples restricted to economical ore bodies.

nanlahti. The Vallitunsaari sample may be a relict from an earlier metamorphism, as discussed below. The Nunnanlahti material may represent lead sulfide remobilized from the 2800-m.y. basement rock that, at this locality, may be at very shallow depth (E. Viluksela, personal communication). The veinlets occur in sheared skarn rock.

Sample 32 from Varpaisjärvi from the old basement gives a model age of about 2600 m.y., in reasonable agreement with the zircon ages of 2600 to 2800 m.y. for these basement granites. Sample 31 from Huhus was presumably contained in basement rock also, but it is a new occurrence that has not been studied in detail. If it actually lies in the basement, it was probably generated from the basement rocks during a later metamorphic event but contaminated with some radiogenic lead.



The most interesting results are those on the larger sulfide accumulations in the Karelian province. Of the six deposits sampled, five carry lead that gives a model age of  $2100 \pm 100$  m.y. within the experimental error. The two

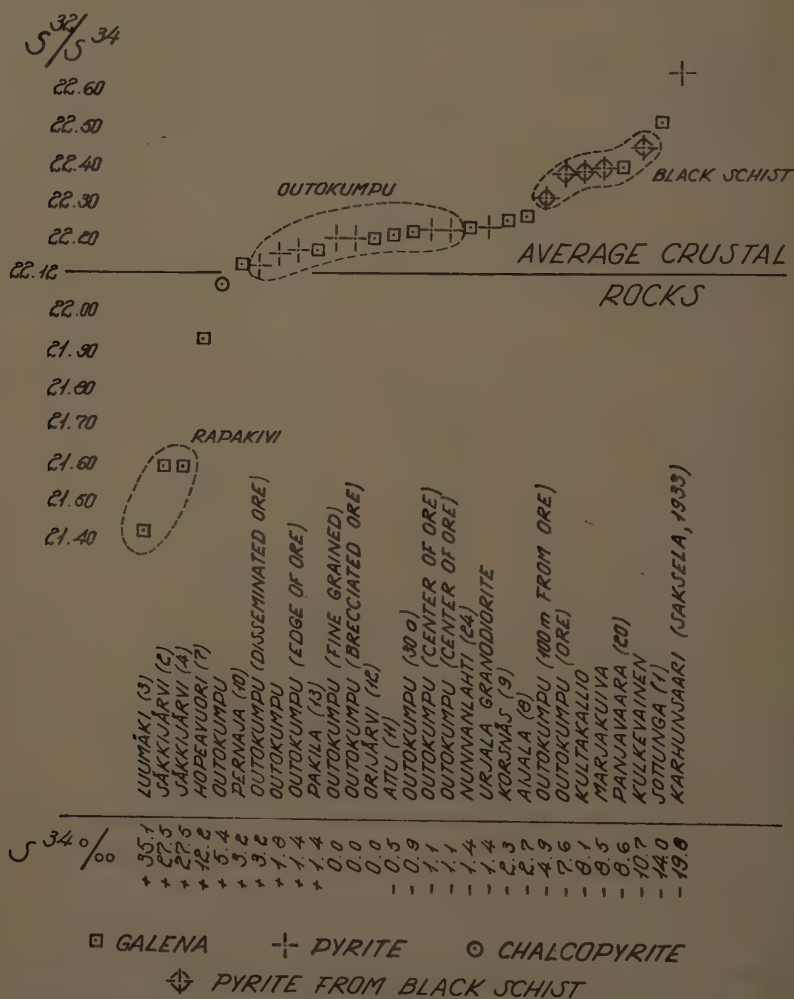


FIGURE 4. Diagram showing the isotopic ratio  $S^{32}/S^{34}$  of some Finnish sulfides.

Outokumpu samples are self-consistent but have model ages that are slightly older (2270 m.y.).

There are several ways of interpreting these results, but the lead-isotope systematics place some boundary conditions on the hypothesis to be used. The fact that these galenas come from significant accumulations, some of them of massive dimensions, would reduce the possibility of significant contamination to the lead.

If it is assumed that the Karelian and Svecofennian geosyncline and metamorphism were synchronous, then the ores must have been emplaced at 1800 m.y. or younger. The model ages would then have to be explained as: (1) remobilized ancient ore bodies from the basement, or (2) lead from peculiar portions of the basement that carried a very low U/Pb ratio. Although possible, neither of these alternatives appears highly probable. Long *et al.* (1960) have established remobilization of older lead ore on a minor scale in the Coeur d'Alene district at the contact of a large Tertiary dike adjacent to a Pre-Cambrian lead ore body. A. I. Tugarinov (personal communication) has observed this phenomenon in a deposit in the Kola peninsula. There are also a few recorded cases where the model age is older than the rocks in which they are found; this has been attributed to a low U/Pb ratio in the source rock. Neither of these anomalies is common, and it is somewhat difficult to accept this as the sole explanation of all of the ore deposits distributed throughout the Karelian rocks in Finland.

Another explanation that could readily account for the 2100-m.y.-old sulfides is that the Karelian province was originally metamorphosed at about 2100 m.y. ago and followed shortly by ore formation. The province was then remetamorphosed at 1800 m.y., when the granites and granodiorites that have yielded the zircon ages were intruded. The former ore bodies were sufficiently inert to be preserved or were only locally remobilized.

One difficulty with this hypothesis is that it would cause a drastic revision in present conclusions concerning the Karelian rocks.

It cannot be readily postulated that the sulfide deposits yielding 2100-m.y. model ages simply reflect lead from a 2800-m.y.-old basement that was in a lower-than-average U/Pb environment and that it was actually emplaced at 1800 m.y. ago. The reason is that galena from these deposits falls along the normal 2100-m.y. isochron, whereas they should have shown an entirely different pattern (see FIGURE 2) if the above hypothesis were true. It is noteworthy that 2100 m.y. is the time of the Belomorian orogeny that widely affected rocks at least in Russian Karelia, the Kola Peninsula, and northeasternmost Finland.

FIGURE 3 is a  $Pb^{208}/Pb^{204}$  versus  $Pb^{206}/Pb^{204}$  plot of all samples representing significant sulfide bodies. These again show the sharp difference between the younger Svecofennidic samples, which apparently also encompass those formed in the Savo schist belt and the apparently older Karelides.

Also shown on the isochron diagram (FIGURE 2) are the two samples from the Petsamo area that appear entirely unrelated to the major metamorphic belts and, if normal, were emplaced in late Pre-Cambrian time.

The samples from veinlets cutting the Rapakivi appear to be essentially modern or, if somewhat older, they contain a significant fraction of radiogenic lead. They clearly were not formed promptly at the close of the Rapakivi intrusion because the lead isotope composition in the potash feldspar of the Rapakivi is normal (Kouvo, 1958).

The sulfur-isotope data help considerably in establishing this point. Note that three of the Rapakivi samples (2, 3, and 4), which are fairly close together, show very heavy sulfur. The Sottunga vein several hundred miles to the west, however, is very light. None of this sulfur could reasonably come from the Rapakivi itself since, in the formation of an igneous granite, the sulfur isotopes

tend to become homogenized at something approaching the average crustal value of  $S^{32}/S^{34} = 22.12$ .

Thus it is possible that both the lead and the sulfur in these cross-cutting veinlets were derived from the shallow basement in fairly recent time. Note that the most radiogenic lead from the Sottunga, which lies far off the isochron diagram, is also accompanied by the very light sulfur. This correlation is generally observed and probably reflects an original environment approaching black shale where both uranium and the light isotopes of sulfur are enriched. It is noteworthy that the Hopeavuori sample 500 m. outside Rapakivi appear to show normal isotopic composition of lead associated with anomalous heavy sulfur (21.94).

FIGURE 4 is a diagram showing the relation of the sulfur data in both isotopic ratio  $S^{32}/S^{34}$  and parts per mil from the meteorite standard. Since most of the Svecofennian and Karelian samples, including the large Outokumpu deposit, lie significantly above the crustal average, this strongly suggests that the sulfur as well as the lead was derived from metasedimentary sources rather than the mantle or the deep basaltic part of the crust.

When all of the lead isotopic analyses are plotted on the geological sketch map (FIGURE 1), a fairly distinct boundary line may be drawn between samples showing the 1800-m.y. and the 2000- to 2300-m.y. model ages, providing the samples originating from small quartz or carbonate veinlets are omitted. This systematic relationship is clearly related to regional geologic features of the Finnish bedrock. The samples giving the 1800-m.y. model ages lie within the Svecofennian area. This same line separates the formations characterized by calcareous carbonates (west) and the dolomites (east) or those poor in quartzites and serpentinites (west) from those rich in these rocks (east). The difference between the Svecofennian and Karelian rocks has been known for a long time. The new isotopic data may suggest that the Karelian province had a history prior to 1800 m.y.

### *Conclusions*

- (1) The Svecofennian province, including the Savo schist belt, yields galenas of uniform model age of about 1800 m.y.
- (2) The Karelian province has lead of two types: galena from small veinlets carry model ages of 1800 m.y., while the large ore bodies average about 2100 m.y. Unless these leads have had an unusual crustal history, they suggest that the Karelian rocks may have undergone more than one orogenic episode.
- (3) Galena samples from the old basement give model ages ranging from 2300 to 2800 m.y.
- (4) The sulfur-isotope composition of the ores in the Svecofennian and Karelian zones suggests that they were derived from metasedimentary sources rather than from the mantle or the deep crust.
- (5) The sulfide veinlets in the Rapakivi granite appear to have been derived in relatively recent time from the old basement below these shallow bodies.

### *Summary*

In order to understand further the complex metamorphic history of the Precambrian rocks of Finland, the isotopic compositions of the lead and sulfur

were determined in a suite of galena samples chosen to represent the major orogenic or igneous events. These data suggest that the Svecofennidic geosynclinal rocks may have undergone only one major orogenic event at about 1800 m.y. ago and that the primary sulfide deposition closely followed the plastic deformation, as is observed commonly elsewhere. Similar model ages are obtained for small veinlets in the Karelidic province, but five larger ore bodies give model ages of 2100, and Outokumpu gives 2300 m.y. This may suggest an earlier history for the Karelian rocks before 1800 m.y. or may represent anomalous lead with an unusual crustal environment. Galena-bearing veins in the Rapakivi granite appear to have been derived from the underlying shallow basement in Phanerozoic time.

### *Acknowledgments*

We are grateful to the Outokumpu Company for permission to use the material collected under the sponsorship of the Exploration Department. Yrjö Vuorelainen assisted in the preparation and optical study of the samples used and E. J. Catanzaro, D. S. Miller, and A. E. Long made some of the isotopic measurements. Numerous geologists have kindly cooperated in procuring critical samples.

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## APPENDIX

The following samples have been described previously (Vaasjoki, 1956; Kouvo, 1958): (1) Pb-231, galena from quartz-feldspar-sulfide vein in Rapakivi granite, Södö, Sottunga; (2 and 4) Pb-174 and Pb-230, samples from galena-bearing veins in Rapakivi granite, Säkki-järvi, Union of Soviet Socialist Republics (former Finnish area); (3) Pb-229, galena from fissure fillings in Rapakivi granite, Luotola, Luumäki; (7) Pb-232, galena from a small ore mineralization, more than one-half kilometer from the contact of Rapakivi, Hopeavuori, Lemi parish; (8) Pb-234, galena from Aijala sulfide deposit, Kisko; (9) Pb-238, galena from a veinlike carbonatite formation, Korsnäs mine, Korsnäs; (10) Pb-235, galena from some sulfide veins, Koskenkylä, Pernaja (Vaasjoki, 1953); (11) Pb-233, galena from a small sulfide mineralization in Attu; (12) A-67, galena from Orijärvi sulfide deposit, Kisko; (13) Pb-175, galena from a small galena mineralization found at Pakila near Helsinki (Kulonpalo, 1946); (18) Pb-240, native lead found from soil in Keihäsjoiki, Juuka (sample originates most probably from the Panjavaara-type veins); (20) Pb-239, galena from a carbonate vein, Panjavaara, Juuka parish; (28) Pb-228 and Ar-48, galena from the Outokumpu mine (Vähätalo, 1953); (29) Pb-247, galena from an amphibole skarn, Nunnanlahti, Juuka.

*Samples 5 (Suolavuono) and 6 (Peuravuono).* These galena samples were received from Lauri Hyvärinen of the Geological Survey of Finland. Both museum samples were connected with a microscopic investigation carried out by Hyvärinen. Labeling was as follows: No. 8799, Suolavuono 4, Petsamo and No. 8804, Edward, Peuravuono, Petsamo. The general geology of these galena occurrences has been described by Hausen (1932). According to this worker (page 20): "The Edward vein runs from the sea coast in an approximate east-to-west direction and has been traced by Hall as far as 1600 m. At one place the vein is crossed diagonally by a fault. At some distance from the sea coast the vein has been metamorphosed in a split fissure by the advancing work of the surf. . . . This vein cuts through a mica gneiss, which is very rich in garnet and is permeated in part by a white pegmatite. The ore minerals in this vein are galena and sphalerite. According to available specimens, which are to be found in the debris on slopes of hills, it appears as if these two sulfides occur separately in the vein. The sphalerite remains closer to the border of the vein while the galena appears as clusters in the middle. The bulk of the vein is quartz partially built of cellular structure." (Editor's translation.) In addition to galena, sphalerite, pyrite, and chalcopyrite have been found, under microscope, in a polished section of Peuravuono material. The Suolavuono material consisted of compact galena ore with a few white unidentified (less than 0.01 mm.) inclusions. Also the Suolavuono (Basarnaja) group has been described by Hausen (1932, pages 15 to 18).

*Sample 14, Yläjärvi, galena from the copper ore deposit of Paronen in Yläjärvi parish.* A general description of the Paronen ore is given by Himmi (1954). According to this investigator, the mineralization has taken place in two almost parallel breccia zones where the angular fragments of the discolored tuffite and porphyrite have been cemented by a mass of ore-bearing black tourmaline. The lithologic association consists chiefly of volcanic tuffites, agglomerates, porphyrites, and quartz-feldspar schists. The surroundings belong to the Svecofennian area. The brecciation has been supposed to be a result of an explosionlike gas outburst (Himmi, 1954). The sample analyzed has been taken 4 to 5 m. above the level 240 from the back part of the breccia zone. This galena originates from a sulfide vein rich



in chalcopyrite and galena. This kind of sulfide veins penetrating ore is not very common in Ylöjärvi mine. This sample, labeled as Y-294, was kindly furnished by Reino Himmi of Ylöjärvi mine.

*Sample 15, Viitasaari, galena sample from garnet-bearing mica gneiss near the Kärnä school, Viitasaari parish.* This sample was furnished by the Geological Survey of Finland. According to Aatto Laitakari (personal communication) this (not economical) deposit has to be considered epigenetic. Sphalerite also has been found. The analyzed sample originates from a specimen rich in pyrrhotite, pyrite, and chalcopyrite. Some accessory ilmenite and rutile have been found. Pyrrhotite is partly altered to pyrite. Mineralization belongs to the western border of the Savo schist zone.

*Sample 16, Pihtipudas, galena from Riiövuo region 2 km. south of Pihtipudas church.* This mineral assemblage contains arsenopyrite and some silver minerals. The mineralized zone cuts volcanic schists and is rich in quartz veins and tourmaline breccia (Aatto Laitakari, personal communication). This sample was obtained from the Geological Survey of Finland. In addition to galena, arsenopyrite, pyrrhotite, chalcopyrite, pyrite, accessory ilmenite and three unidentified sulfosalts have been found microscopically. Silver and a trace of bismuth have been found in the X-ray fluorescence spectra.

*Sample 17, Säviä, galena from a quartz vein found in an ore boulder originating from a small sulfide deposit at Säviä in Pielavesi parish.* Säviä region is characterized by striking cordierite-anthophyllite-garnet gneisses cut by different kinds of plutonic rocks. One of those intruding the Savo schist belt east of Säviä, the hypersthene granite of Vaaraslahti, has been dated at around 1800 m.y. (Wetherill *et al.*, in press). This sample was obtained from a quartz vein cutting the small sulfide deposit in the Savo schist belt. Some sphalerite and chalcopyrite have been found under the microscope in the patches of pyrrhotite, magnetite, and galena. Pyrite occurs as large crystals in pyrrhotite.

*Sample 19, Kiiminki, galena found associated with chalcopyrite and iron sulfides in a vein-like quartz patch in phyllite.* This sample, found at Kotajärvi of Kiiminki parish, was forwarded from the Geological Survey of Finland (the general features of the local geology appear on the General Geological Map of Finland, 1:400,000, Sheet C5-B5, Oulu-Tornio [Geologinen tutkimuslaitos]).

*Sample 21, Kuurna, galena from Kuurna canal, Paihola, Kontiolahti parish.* This sample has been taken from quartz veins and patches in typical Karelian mica schist penetrated by intrusive rocks of 1800-m.y. age. In addition to galena, some pyrite, sphalerite, and chalcopyrite were found. Microscopic examination showed a few bright white inclusions in galena. The sample was kindly collected by Erkki Viluksela of the Exploration Department of the Outokumpu Co.

*Sample 22, Vallitunsaaari, galena from a quartz-calcite vein in diabase, Vallitunsaaari, Laurila, Kemi.* This rock is part of the Kemi area described by Härme (1949), who states that this rock is a variety of greenstone characteristic of Karelian formations. In the Kemi area the greenstones range from fine-grained basalt with amygdaloidal texture to fairly coarse-grained diabases and gabbroic varieties. The greenstone at Vallitunsaaari contains also layers of quartzite supposed to be inclusions. This sample is the only exception to the rule that galenas collected from vein formations in the Karelian province show an age of 1800 to 1900 m.y. Vallitunsaaari galena belongs to the same group as those from the Karelian sulfide deposits. Except for inclusions in the chalcopyrite, galena forms a vein within it. Some pyrite grains occur in chalcopyrite, as do some chalcocite and covellite. Sphalerite as well as magnetite is common. A small bismuth grain has been found in galena.

*Sample 23, Ahmovaara. A small carbonate patch with galena was found in serpentinite on the shore of Lake Pielinen, Ahmovaara, Juuka parish.* This rock belongs to the basement complex underlying the Karelian schists; the galena sample belongs to those taken from small veins and patches that form a group showing an age of around 1800 to 1900 m.y. This sample also was obtained from Viluksela.

*Sample 25, Pyhäsalmi.* The Pyhäsalmi sulfide deposit (owned by the Outokumpu Company) is located on a narrow neck between the lakes Pyhäjärvi and Komujärvi in Pyhäjärvi parish. The deposit, found in the fall of 1958, is characterized by massive sulfides of pyrite, pyrrhotite, sphalerite, and chalcopyrite. Some disseminated galena was found in the drill hole PyO-3 (121.70 m.), section x = 15.400. The wall rock consists of mica gneiss with some interlayered skarn beds. Galena was situated in the footwall of the central part of the ore body. The second sample was obtained from the drill hole PyO-5 (79.07 m.). These samples were furnished by Olavi Helovuori of the Pyhäsalmi mine.

*Sample 26, Vihanti.* The first sample (206/204 = 15.08) represents a compact galena ore from Vihanti ore. Large chalcopyrite and pyrrhotite inclusions have been found in massive galena. In addition sphalerite, tetrahedrite, gudmundite, and secondary marcasite have been found microscopically. The second sample (206/204 = 15.20) originates from the 200 level (x = 5984, y = 1705, and z  $\cong$  197) and aside from galena contains some sphalerite, tetrahedrite, boulangerite, chalcopyrite, pyrite, and arsenopyrite. Some small uraninite grains

have been found. These accessory uraninites occur in silicates, and some chalcopyrite has been concentrated in the pleochroic halo. Small amounts of uraninite, possibly an impurity, might explain the slight difference between the Vihanti samples. The general geology of the Vihanti zinc deposit has been described by Isokangas (1954). Several observations point to an epigenetic kind of ore.

*Sample 27, Pattijoki.* Approximately 12 km. east-southeast of the city of Raahe, in the northwest end of a schist belt, a drill hole can be seen marked on the Geological Map of Finland (1:100,000, Sheet 2441, Raahe, Geological Survey of Finland). It is located at Ylipää, a village of the Pattijoki parish. Between amphibolite and mica, gneiss skarn (about 30 cm.) along with some of the sulfides including galena and sphalerite were found. This sample was obtained from the Geological Survey of Finland and the geological information was furnished by Eero Pehkonen.

*Sample 28, Petrovaara.* The systematic prospecting carried out by the Exploration Department of the Outokumpu Company led to the discovery of a small, not economical, sulfide deposit at Petrovaara, Juuka parish. The mineral assemblage consists of pyrite, pyrrhotite, and a small amount of chalcopyrite, sphalerite, and galena. These sulfides are situated within the Karelian schist belt (Frosterus and Wilkman, 1920). A galena sample for analysis was received from Erkki Viluksela of the Outokumpu Co.

*Sample 29, Pitkäranta.* Three museum samples have been selected from the ore fields of Pitkäranta: (1) Lupikko, Impilahti; (2) Herberz I (New Mining Field); and (3) Beck, Hopunvaara. Since the Pitkäranta area no longer belongs to Finland, field observations were not possible. However, several earlier detailed studies are available. The classical research by Trüstedt (1907) gives the general geological features as well as the details of the occurrences. More recently Eskola (1951, 1952) and Saksela (1951, 1952) have discussed the genetic circumstances controlling the ore material and the ore carrier problem at the Pitkäranta region.

*Sample 30, Outokumpu.* The first analysis (30a in TABLE 1) was made by the lead tetramethyl technique and by the surface emission, the second (30b) by surface emission. The agreement is considered good. The first sample (30a) originates in the center of the ore body from a vein rich in chalcopyrite in the breccia-type ore. The new analysis (30b,  $206/204 = 14.77$ ) has been made on galena found in the V area in the contact zone of ore against serpentinite and skarn rich in diopside. The mineralogy of this rock differs markedly from that of the chief ore types, being especially rich in sphalerite and accessories. In addition to chalcopyrite, pyrite, pyrrhotite, sphalerite, and galena, stannite, gudmundite, bismuth, gold, chalcopyrite, cobaltpentlandite, and eskolaite have been found. Some uraninite and thucolite also have been found in this 50- to 30-cm.-thick contact zone of ore.

*Sample 31, Huhus.* At Huhus in Ilomantsi parish in eastern Finland the Malminetsijä Exploration Company has decided to proceed with a study of a galena mineralization that was found in the pre-Karelian basement area east of the Karelian schist belt. One sample was received from A. A. T. Metzger for isotope work. According to Metzger, galena is impregnated in the gray basement gneiss common in that region. Some sphalerite, pyrite, and ilmenite with galena mineralization were found in a microscopic examination.

*Sample 32, Varpaisjärvi.* Some galena in an aplitic granite was found in digging a well at Mantila, Lukkarila, Varpaisjärvi parish. This sample, sent to the Geological Survey of Finland, was forwarded to us for isotope work. The geology of this sample is poorly known. As may be seen from the General Geological Map of Finland (1:400,000, Sheet C3, Kuopio), this region is a part of the older granite-gneiss basement underlying the schists of Kuopio region.

### *Discussion of the Paper*

**KULP:** The Soviet work has covered the entire Baltic Shield area from southwestern Norway to the Kola Peninsula, not merely a small area in eastern Karelia. The fact that the measurements were done by the volumetric method does not invalidate them, particularly as I observed on a visit to E. K. Gerling's laboratory that they are normally run in duplicate with different quantities of sample. To check their absolute calibration, A. A. Polkanov kindly gave me a sample of separated muscovite from their most ancient rocks of the Kola Peninsula on which they had obtained 3400 m.y. using our decay constants. We ran this at Lamont using our standard isotope-dilution technique and obtained the same result within the experimental errors of both measurements.

The K-Ar measurements are self-sufficient in determining reliable minimum

ages. The presence of 2600- or 3400-m.y.-old biotite or muscovite clearly established an ancient basement without measurements by other methods. However O. Kouvo, elsewhere in this monograph, has certainly put the detailed interpretation of the Svecofennidic-Karelian orogenies on a firmer basis by his Rb-Sr and zircon measurements.

R. D. RUSSELL (*University of British Columbia, Vancouver, B. C., Canada*): I have only two comments I'd like to make. One I make with some hesitation. Although I do not know about the lead-isotope analyses the Soviets are currently doing, I do know that many of us felt that there was a very large uncertainty in  $Pb^{204}$  in the earlier measurements.

The second comment is that I have some reservations about using common lead data for dating galenas without a rather detailed study of the isotopic and geological relationships.

P. W. GAST (*University of Minnesota, Minneapolis, Minnesota*): It should be pointed out that the galena analyses reported by Kouvo were not made by Soviet geologists but were made at Lamont.

Whether you believe the model is really immaterial here, it still distinguishes the galenas from each other.

M. N. BASS (*Carnegie Institution of Washington, Washington, D.C.*): Without meaning to detract from anyone, permit me to point out that the age work on the mantled gneiss domes, both in Karelia and in the Baltimore area, has served merely to confirm the interpretation of mantled gneiss domes that Eskola proposed on purely geological grounds.

## THE PRE-CAMBRIAN GEOCHRONOLOGY OF THE BALTIC SHIELD

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### *Introduction*

Our present more advanced experience on the geochronology of the Baltic Shield is based on 540 age determinations of micas done chiefly by the K-Ar method. There are about 400 age determinations for the Kola Peninsula and Karelia, Union of Soviet Socialist Republics, and about 150 determinations for Finland, Sweden, and Norway, made in collaboration with geological surveys of these countries.

New data confirm our geochronological division of the Baltic Shield, made one year ago, into two parts: the eastern and oldest major part, to which we may adjoin now the Russian Platform and Ukrainian Shield or the Sveco-Fenno-Sarmatian Shield; and the second minor part, the Gothian-Ryphean-Caledonian folded belts, which surround the former.

The final consolidation of the oldest Pre-Cambrian part of the Shield was completed as a result of the Karelian-Sveco-Fennian diastrophism 1850 to 1640 m.y. ago that was preceded by five to six earlier folding (orogenic) periods.

The second girdling-folded belt was formed during the Gothian-Ryphean-Caledonian periods of diastrophism 1570 to 405 m.y. ago.

The first and oldest part of the Shield at the time of these folding periods existed as a great Gothian-Ryphean-Caledonian Platform—Shield with a very complicated structure (FIGURE 1).

### *The Oldest Part of the Shield: 3500 to 1640 m.y.*

*The Pre-Cambrian.* This oldest part of the Baltic Shield may be divided according to absolute-age geochronology into six or seven geosyncline cycles. Beginning from the oldest, these cycles are: the Katarchean, the relics of formations of one to two cycles; the Lower Archean-Saamian, with two cycles; the Upper Archean-Belomorian; and the Sveco-Fennian-Karelian with Lower- and Upper-Karelian cycles.

*The Katarchean: 3500 to 3000 m.y.* The gneisses of the Katarchean have been discovered as relics among migmatites, granites, and pegmatites of the same age in the northeastern part of the Kola Peninsula, considered to be the basement for the Lower Archean-Saamian formations—Polmas and Poros. Outcrops of the Katarchean have been discovered in an area  $50 \times 12$  km.

Conventionally the Katarchean is divided into the Lower Katarchean: the gneisses, granites, and pegmatites of 3500 to 3250 m.y., and the Upper Katarchean: the granites of 3100 to 3000 m.y.

*The Lower Archean-Saamian formations: 2870 to 2150 m.y.* These extensive developments on the Kola Peninsula and elsewhere have been discovered to be a basement of the Karelides in the same region as well as in central and North Karelia and Finland.

The xenoliths of Saamian gneisses have been discovered in the Upper Archean-Belomorian of north Karelia.



Thus the Lower Archean-Saamides with the relics of the Katarchean have formed the frame and the basement of the Upper-Archean-Belomorides and Karelides (Kola Peninsula and Karelia, Finland).

To the Lower Archean I (I Saamides) belong the iron ore gneisses of Olene-gorsk (2530 m.y.), the Polmas formation (2870 to 2530 m.y.), and the granite complex (2870 to 2500 m.y.). To the Upper Saamides belong the Poros gneisses (2370 to 2200 m.y.) and the granite complex (2490 to 2100 m.y.).

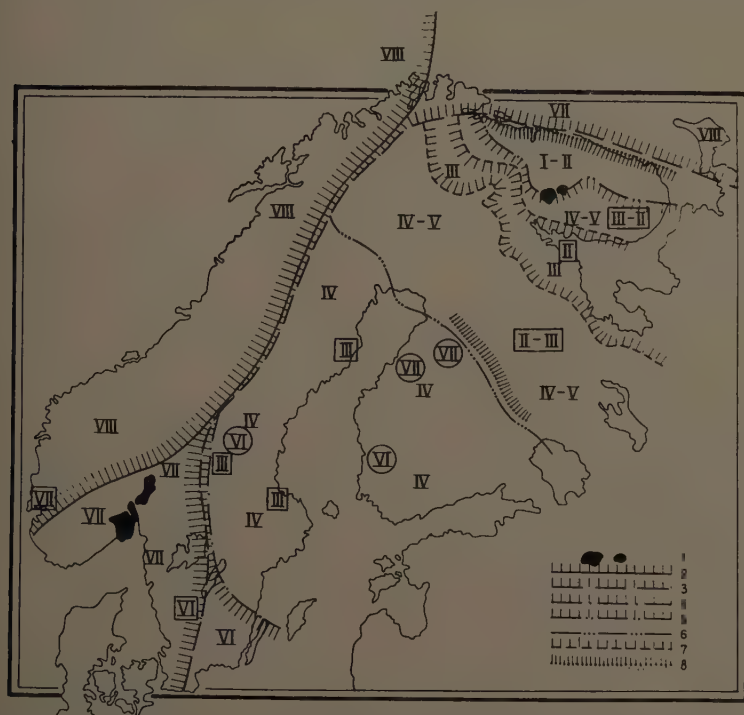


FIGURE 1. The Baltic Shield: Schematic geochronological division of the Pre-Cambrian. (1) Palaeozoic alkaline intrusions. (2) Boundary of Caledonides (the shade is directed inside of the folded belt). (VIII) The Caledonides. (3) Boundary of Ripheides. (VII) The Ripheides. (4) Boundary of Gothides. (VI) The Gothides. (5) Boundary of Sveco-Fennides-Karelides. (IV) The Sveco-Fennides. (IV and V) Upper and Lower Karelides. (6) Inner boundary between the Sveco-Fennides (IV) and the Karelides (IV and V). (7) Boundary of the Intermontanes of Belomorides. (III) The Belomorides. (8) Boundary of Saamides. (II) The Saamides. (I) The Katarchean. (Numbers in rectangles—formations in basement, same in circles—platformic.)

The first period of alkaline rock complexes (syenites and granites, 2300 m.y.) and also the rare metal pegmatites (2300 to 2100 m.y.) of the Kola Peninsula belong in this period.

*The Upper Archean-Belomorides of Karelia: 2100 to 1950 m.y.* The Belomorides form the wide folded belt stretching northwest on both sides of the White Sea to the Caledonian ranges of Scandinavia. To the Belomorides belong the gneissic complex (2100 to 1900 m.y.), the Belomorian granites (1950 m.y.), and the enormous massif of granulite (1980 to 1860 m.y.) on the Kola Peninsula.



Gneisses and granites with the same ages as the Belomorides (2025 to 1925 and 2100 to 2050 m.y.) have been discovered in the basement of the Karelides in various parts of the Kola Peninsula.

Lastly the Upper Archean age has the schists of Skelleftea (2140 to 2050 m.y.)\* and the oldest granites of Uppsala and Borlange (1950 m.y.) in northern Sweden.

Thus the Belomorides—gneisses, granites, and granulites—with relics of the Lower Archean have formed a wide folded belt amid the older Lower Archean-Saamides. The Belmorian granites have also intruded into the Saamides and have been discovered in the basement of Sveco-Fennides of Sweden and of Karelides in different places.

*The Sveco-Fennides-Karelides: 1870 to 1640 m.y.* These, the youngest of the geosyncline Pre-Cambrian formations in the Sveco-Fenno-Sarmatian Shield, are spread chiefly in Sweden and Finland, while the Karelides are found chiefly on the Kola Peninsula, in Karelia, and in northern Sweden and Norway. The Lower Karelian of the Kola Peninsula, Karelia, and Finland is older than the synkinematic post-Karelian granites. The Upper Karelian-Jatulian is older than the rapakivi granites (1640 m.y.).

In the basement of the Karelides were discovered the Lower and Upper Archean in Karelia, Kola Peninsula, and in Finland. In the basement of the Sveco-Fennides of Sweden were discovered Upper-Archean schists and granites.

The metamorphism of the supracrustal Lower Karelides has the varied ages of 1770 m.y. in Finland, 1850 to 1750 m.y. in Karelia, and 1790 to 1720 m.y. in the Kola Peninsula; the metamorphism of the Sveco-Fennian gneisses is given as 1770 to 1730 m.y. in Finland and 1780 to 1640 m.y. in Sweden.

The age of post-Karelian granites is 1860 to 1650 m.y. in Finland and 1860 to 1620 m.y. in Karelia and the Kola Peninsula. The age of the Sveco-Fennian granites is 1840 to 1610 m.y. in Finland and, in three groups of Swedish granites, 1880 to 1800, 1770 to 1700, and 1680 to 1615 m.y. The age of the last of the Swedish granites is similar to that of the postkinematic rapakivi granites of Finland, that is 1640 m.y.

The age of the metamorphism of the iron-ore gneisses of northern Finland, western Karelia, and the Sveco-Fennian iron-ore gneisses of southern Finland is similar to that of the metamorphism of the Upper Karelian.

On the other hand the Lower Karelian iron-ore gneisses of western Karelia are initially older than the age of the metamorphism and of intruding granites (1880 to 1770 m.y.) but younger than the age of the granite from a boulder in the basal conglomerates (2540 m.y.)

To the late Karelides belongs the second epoch of alkaline intrusions of the Kola Peninsula and of Karelia (1880 to 1680 m.y.).

The proximity of the absolute age of the rapakivi granite complex and alkaline complex is noteworthy. It is very significant that the alkaline complexes are widespread in the northeastern belts of the Karelides on the Kola Peninsula and in Karelia, while the rapakivi granites complexes occur in the southern belts of Sveco-Fennides mainly and, partly, in the southern Karelides of Karelia.

\* Preliminary total-age determinations by K-Ar.

With the intrusion of rapakivi and alkaline complexes, the chief and final consolidation of the oldest eastern and principal part of the Sveco-Fenno-Sarmatian Shield (1640 to 1610 m.y.) took place.

*The Folded Belts of Gothides-Rypheides-Caledonides (1570 to 405 m.y.)  
and The Gothides (1570 to 1120 m.y.)*<sup>4</sup>

*The Gothian-Caledonian platform.* This immense platform was surrounded on the northwest, northeast, and east by belts of the younger folded ranges of the Gothides-Rypheides-Caledonides, for which we have at present considerable geochronological data.

*The Gothides of southern Sweden.* These were formed at an interval of 1570 to 1120 m.y. and probably can be divided by granite intrusions into two or three periods.

Gothides I of southern Sweden (1570 to 1420 m.y.) are the coast gneisses in the orogenic belt of Karlskrona (1560 m.y.) and the schists of the island Uto (1570 m.y.) into which the Smöland granites of Kalmar (1475 m.y.). Twing (1460 m.y.), Karlshamn (1420 m.y.) and Vetland (1560 m.y.) have intruded. The Karlshamn granites are postkinematic and have intruded into the Kalmar and Twing granites.

The Gothides II (1380 to 1185 m.y.) formations are preserved in southern and middle Sweden.

The mica quartzites of Solvesborg (1270 m.y.), the schists of Filipstadt series (1275 m.y.),\* and the Grythyttan series (1380 m.y.)\* belong to the orogenic formations of Gothides II. The Jotnian pelites northwest of Falun in northern Sweden (1185 m.y.)\* and siltstone at Muhos, Finland (1284 m.y.)\* have a near age, but belong to the relics of the platform formations of Gothides II. The typical Gothian Karskoga granites (1260 to 1270 m.y.) and Vaggerid syenites (1270 m.y.) have completed the Gothian II orogenic cycle.

The oldest Chatkalskaya series of the Timan range (1130 m.y.),\* the Askim granites of Göteborg (1135 to 1120 m.y.) and the Jotnian siltstone of northern Finland (1130 m.y.)\* may belong therefore to orogenic and platform formations of still younger Gothides (Gothides III?).

*The Rypheides*

*The Ryphean and Rypheides (1080 to 715 m.y.).* We have defined the geochronological position of the Ryphean on the basis of the absolute age of the formations of Rybachy (Fishers) Peninsula and Kildin Isle. The Ryphean period is divided by the acid intrusions into two parts.

Ryphean I (1080 to 900 m.y.) consists of the series of the Sredny Peninsula (920 m.y.)† and of Kildin Isle (1010† and 1030\* m.y.) both of which represent the relics of the marginal part of the Ryphean geosyncline, which was located to the north of the Kola Peninsula.

The broad belt of Rypheides has been discovered by radiological data in the gneiss belt of southern Norway and Sweden. Here it is possible to distinguish three structural zones: (1) the orogenic zone of gneisses and schists; (2) the

\* The preliminary total-age determinations were made by K-Ar.

† Age by glauconite.

zone of the protruding basement, rejuvenated to the age of Ryphean I; and (3) the Ryphean schists in the belt of the Ryphean I platform.

The broad orogenic belt consists of the Bamle gneisses of southern Norway (1052 to 900 m.y.), the Marstrand gneisses of southern Sweden (1066 to 1040 m.y.), and the Dala series of southern Sweden (1025 m.y.).\* We believe that "the schistosity zone of Småland and Scania" on N. H. Magnusson's geological map also was formed at the period of formation of Rypheides I (or I and II).

The rejuvenated basement (or the intermontane block) has a width at 110 to 120 km. and is located between the orogenic and the schistosity zones (the width of these zones being 100 to 150 km. in Norway and 200 to 250 km. in Sweden).

The crystalline basement has partly an autonomic geological structure not related to the principal structure of Rypheides I, but geochronologically it is of the Ryphean age of metamorphism, 1070 to 940 m.y. (eight age determinations).

Last in order on the Ryphean platform with a basement of crystalline Sveco-Fennides and Gothides in grabens and depressions of southern Sweden are found the schist formations of the Visingsö series (985 m.y.) and the Almasätra Series (964 m.y.), the platformic formations of Ryphean I.

The Ryphean I gneisses have been penetrated by Birkeland granites 1030 to 905 m.y. (Rb/Sr = 966 m.y.) and Flö granites, 997 to 943 m.y., in the Norwegian part of the orogenic zone.

To the Swedish part of the orogenic zone belong the Kroppe, Amal, and Filipstad granites (1082 to 1060 m.y.) and the gneiss-granites of Karstadt (992 m.y.) in the basement.

The postkinematic Bohus granites of Sweden (1010 m.y.) and Ostfold granites of Norway (776 to 823 m.y.) may belong to either the Rypheides I or II.

The Rypheides II (890 to 770 m.y.) have been determined by the age of metamorphism of the orogenic formation of Rybachy Peninsula (890 to 715 m.y.).\*

All samples of Telemarken gneisses (890 to 824 m.y.) and the intruding Telemarken granites (772 to 777 m.y.) in southern Norway have almost the same age.

Some granites from the Bamle gneiss area (Ryphean I) have an age of 885 to 880 m.y.

These granites, as well as the Ostfold-Bohus granites that probably belong to Rypheides II also, have intruded into the consolidated gneisses of Rypheides I (that is, into the consolidated basement of Rypheides II).

A sample of Sweden Sparagmite, from a tectonic block or plate within the Caledonides, shows an age of 560 m.y.,\* that is, a Cambrian or Caledonian age of metamorphism for this rock.

Thus the age of Sparagmitian of northern and southern Norway is unknown. The structural similarity of the Ribachy Peninsula Ryphean to the Sparagmitian of Finmarken leads us to assume that these formations have the same age.

Thus the structural relations of the Sparagmitian to Ryphean I and II in southern Norway suggest that the Sparagmite are younger than the Ryphean

\* The preliminary total-age determinations by K-Ar.

of this district. This geological problem remains for future geochronological investigations.

The age of Kaolinite (700 m.y.) from Betsäskylö Taivalkoski in northern Finland shows that the Upper Ryphean platform had a mild continental climate.

We adopt the absolute age of Sinian of China, 680 m.y.\* (our determination) as the upper limit of the Ryphean.

#### *The Caledonides: 620 to 405 m.y.*

We have adopted as the lower limit of the Caledonian cycle (in the platform origin) the absolute age of the lower Cambrian blue clay of Leningrad (620 to 610 m.y.).†

For the Kanin-Timan orogenic belt we have determined the age of metamorphism of the schists of the Kanin range (620 to 500 m.y.) and for the upper series of schists of the Timan range (640 to 541 m.y.).

The age of the Swedish Sparagmitian (560 m.y.) also belongs to the Caledonian cycle.

The acid intrusions of the Caledonides are divided into two groups.

*The early acid intrusions: 610 to 535 m.y.* These include the granites of Kanin (550 to 535 m.y.), of Timan (610 to 585 m.y.), and the pegmatites of the intermontane blocks of the Norwegian Caledonides (590 to 582 m.y.).

*The late acid intrusions: 450 to 405 m.y.* These include the trondheimites in the orogenic belt of Norwegian Caledonides (405 m.y.) and the pegmatites of Bergen (450 to 434 m.y.).

Many alkaline intrusions of Norway, Karelia, and the Kola Peninsula belong to the Caledonian Platform of the Baltic Shield. There are early alkaline intrusions of the Fen district in Norway (603 to 590 m.y.) and of the Kandalaksha Fjord in Karelia (518 to 512 m.y.).

To the late group belong the alkaline intrusions of Africanda (425 to 407 m.y.) and Kontosero (410 m.y.) on the Kola Peninsula, of Vuorijärvi (402 m.y. in Karelia), and of Sibljärvi (393 m.y.) and Cap Tury (393 to 294 m.y.) on the Kola Peninsula.

The late acid and alkaline intrusions with an age of about 400 m.y. complete the Caledonian cycle.

#### *The Hercynides*

Vertical movements and deep faulting accompanied by intensive alkaline magmatism also took place in the Hercynian time.

Here is found the alkaline complex of Oslo (315, 308 to 259 m.y.) the intrusions of which were related to Variscian movements of western Europe. The gigantic central subvolcanoes of Chibina and Lovosero (300 to 296 m.y.) have been connected with the orogenic movements of Uralides in eastern Europe.

Thus the alkaline intrusions of the Sveco-Fenno-Sarmatian shield-platform were emplaced during the interval 603 to 303 m.y., periodically arising in connection with the periodic mechanism "*Hebung, Spaltung, und Vulkanismus*" (according to H. Cloos) in the Caledonian and Hercynian Platform.

\* The preliminary total-age determinations by K-Ar.

† Age by glauconite.



*General Conclusions*

The geochronological investigations of the Baltic Pre-Cambrian have made this report possible.<sup>1-3</sup> Similar to the paleontological method of stratigraphy introduced about 170 years ago by W. Smith, absolute geochronology will play a decisive role in the geochronological division, especially of the Pre-Cambrian and, in general, of the entire geological history of the earth.

The geochronology of the Baltic Pre-Cambrian shows that the folded ranges of Lower Archean-Saamides (2800 to 2306 m.y.) with relics of Katarchean blocks (3500 to 3000 m.y.) have formed the oldest sialic continent of the Baltic. This oldest continent has grown by the creation of the folded ranges of the Upper Archean-Belomorides (2150 to 1950 m.y.) and, finally, of the Sveco-Fennides and Karelides (1870 to 1640 m.y.) when the consolidation of pre-Gothian geosynclines and the creation of the vast Gothian-Ryphean-Caledonian platform was completed.

The subsequent growth of the sialic continent continued by the formation of the girdling folded ranges of the Gothides-Rypheides-Caledonides (1570 to 405 m.y.) when the integral continent—post-Caledonian platform-Baltic Shield—originated.

Pre-Cambrian geochronology shows that, instead of an enormous hypothetical Pre-Cambrian hiatus, there were no less than 10 to 12 periods of denudation and sedimentations connected with the formation of geosynclines and folded mountain chains.

We may say that there existed neither an enormous hiatus nor the hypothetical pangeosyncline and panplatform as was believed by some geologists until now.

Aside from this consideration, the similarity of the structural features of the Pre-Cambrian and younger geosynclines allow us to show the eugeosyncline and miogeosyncline belts in the Lower Archean, Saamides-Polmas, (2500 m.y.), in the Upper Archean, the Belomorides, (2150 to 1950 m.y.), and in belts of Karelides and Sveco-Fennides (1870 to 1680 m.y.).

P. Eskola and C. Wegmann long ago established the alpinotype tectonics of different belts of the Karelides in Finland.

The deeper sections of the Sveco-Fennian, Belomorian, and Saamian folded belts sometimes show a similarity to alpinotype tectonics or have structures related to plastic deformations in deep-seated zones.

At the present time these interesting structures are being studied by geologists in many countries.

The above statement indicates that the absolute geochronology confirms the principles of actualism of C. Lyell and J. Sederholm for the known enormous period of Baltic Pre-Cambrian.

In the Baltic Pre-Cambrian are established 13 to 14 intrusive periods of acid and alkaline magmatism.

Two cycles of Pre-Cambrian alkaline magmatism in the Karelian time (1700 to 1600 m.y.) and in the Saamian time (2300 m.y.) indicate that alkaline magmatism is controlled by geological conditions and does not depend on geological age as was thought by some geologists.

For many of the 10 to 12 geochronological epochs of acid magmatism, the



evolution from diorites-granodiorites-plagiogranites to the K-granites has been established. The formation of anchieutectic granites is the principal physico-chemical feature of all these processes. These processes have been connected with anatexis and differentiation but not with metosomatic granitization phenomena.

In addition, absolute geochronology does not confirm the dependence of the degree of metamorphism on geological age.

Thus "the measure and number" or the absolute geochronology at present resolves questions of the division and stratigraphy of Pre-Cambrian and younger formations and may lead to correct resolutions of many theoretical problems of geology.

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# THE GEOLOGIC AGE OF PRE-CAMBRIAN ROCKS OF THE UKRAINIAN AND BALTIC SHIELDS

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This paper represents an attempt to reconstruct a picture of the sequence of events in the formation of the Ukrainian and Baltic shields and the Pre-Cambrian crystalline basement of the Russian Platform connecting them, on the basis of absolute age determinations.

In evaluating the age determinations thus far obtained, of which there have been more than 500 for the territory under consideration, we started from the following basic principles:

The most reliable values are those obtained by applying the Pb-U-Th method to accessory minerals (such as monazite, orthite, and zircon) in those cases where there is excellent agreement among all the ages based on the various isotope ratios.

Where differences exist, usually in the sequence

$$T \frac{\text{Pb}^{207}}{\text{Pb}^{206}} > T \frac{\text{Pb}^{207}}{\text{U}^{235}} > T \frac{\text{Pb}^{206}}{\text{U}^{238}} \gg T \frac{\text{Pb}^{208}}{\text{Pb}^{232}}$$

preference must be given to the value  $T(\text{Pb}^{207}/\text{Pb}^{206})$  as long as the content of radiogenic lead is not so low or contamination with ordinary lead so great that substantial errors are introduced in determining it.  $T(\text{Pb}^{208}/\text{Th}^{232})$  (according to our concepts, which have been confirmed by investigations in areas where distinct recent metamorphism has been demonstrated) indicates the earliest age limit for the most recent metamorphism the given mineral has undergone. As confirmed by experiments on the influence of various solutions on uranium minerals at high temperatures and pressures, under these conditions there occurs selective removal of radiogenic lead with a possibility of partial mobilization of uranium and with thorium remaining totally inert. The thorium/lead ratio is thus the most sensitive to any sort of hydrothermal changes in the mineral connected with the removal of lead and, in fact, dates the earliest age limit for such an event. This fact creates a specific interest in such "divergent" ages.

Another factor, no less important, is dating by the K-Ar method, which also permits us in general to date the most recent metamorphism to which the given rock strata have been subjected.

A considerable amount of experience with investigations of this sort in various regions of the U.S.S.R. has taught us to use K-Ar age measurements with certain reservations and to consider the ages so obtained as only an upper limit for the probable true age of rocks unless they have been confirmed in parallel studies by the Pb-U-Th method.

The problem of interpreting the discrepancies often displayed between ages obtained by the Pb-U-Th and Ar-K methods remains unresolved. Does the Ar-K age correspond to the time of metamorphism, or is it an indication of a

partial thermal influence of much more recent metamorphism that has not resulted in complete recrystallization of the rocks or in 100 per cent removal of argon?

Individual determinations by the Sr-Pb method of the age of micas in cases where the ages have first been determined by the Ar-K method generally have shown similar or greater ages that coincide, in instances where it is possible to check, with ages given by the Pb-U-Th method.

In only one district showing clear recent hydrothermal activity and distinct migration of alkalis (potassium metasomatism) have absurdly high ages been obtained locally by the Sr-Pb method, demonstrating the possibility of a substantial distortion of ages, probably as a result of selective mobility of rubidium.

As a very crude dating method, we have also used the method of ordinary lead, which permits us to date the time of sedimentation of the substance of ancient metamorphic strata. In the evaluation of the ages so obtained, we gave preference to the isotope ratio  $Pb^{208}/Pb^{204}$ , which is less frequently characterized by anomalies than  $Pb^{206}/Pb^{204}$  and  $Pb^{207}/Pb^{204}$ , since the geochemical stability of thorium is greater than that of uranium.

In calculating ages we have started from concepts of the evolution of the isotopic composition of the lead in the earth's crust from the "primary" (meteoritic) lead of 4.5 billion years ago to that of the present, for which we have adopted the lead of Pacific Ocean silts.

The numerical formulas we have obtained are very similar to those proposed earlier by Collins *et al.*<sup>10</sup>

$$Pb^{206}/Pb^{204} = 18.93 - 9.44 (e^{0.154t} - 1) \quad 1$$

$$Pb^{207}/Pb^{204} = 15.72 - 0.068 (e^{0.972t} - 1) \quad 2$$

$$Pb^{208}/Pb^{204} = 38.80 - 37.00 (e^{0.0499t} - 1) \quad 3$$

where  $t$  is the age of the lead-bearing mineral, in billions of years, and  $Pb^{206}/Pb^{204}$ ,  $Pb^{207}/Pb^{204}$ , and  $Pb^{208}/Pb^{204}$  are the isotope ratios in lead.

In those cases where the age determination was made from lead taken from nonlead minerals and there was a risk of adding radiogenic lead isotopes as a result of the dissemination of small amounts of uranium and thorium in these minerals, the isotopic analyses yielding the smallest content of radiogenic lead isotopes were used for the calculation.

The most characteristic determinations of absolute age for the great magmatic complexes or metamorphic strata are presented in the tables accompanying this paper (TABLES 1 to 6).

As a basis for consideration of the Pre-Cambrian history of this large region, we have added a schematic map of the crystalline basement (FIGURE 1), assembled from highly disparate data for the individual portions of the region: a geochronological scheme of the subdivisions of the Ukrainian Pre-Cambrian,<sup>1</sup> a scheme of the superficial structure and data on the age of the crystalline basement of the Russian Platform,<sup>2</sup> and materials on the absolute age of the Pre-Cambrian of the Baltic Shield.<sup>3,8</sup>

The most curious result of investigations of the recent period has been the

TABLE 1

AGES OF PRE-CAMBRIAN ROCKS OF UKRAINIAN AND BALTIC SHIELDS ACCORDING TO DATA OF THE U-Th-Pb METHOD

No.	Mineral and geologic description	Site	Content (% by weight)			Isotopic composition of lead				Age (m.y.)				Assumed age (m.y.)
			Pb	U	Th	Pb <sub>204</sub>	Pb <sub>206</sub>	Pb <sub>207</sub>	Pb <sub>208</sub>	Pb <sub>207</sub> /Pb <sub>206</sub>	Pb <sub>206</sub> /U <sub>238</sub>	Pb <sub>207</sub> /U <sub>235</sub>	Pb <sub>208</sub> /Th <sub>232</sub>	
	<i>Ukrainian shield</i>													
(1)	Orthite from migmatites of Dnieper gneisses	Repyakhivka, Saksgan River	0.12	0.026	0.86	0.01	8.11	1.60	90.29	2760	2410	2630	2630	2700 ± 100
(2)	Orthite from migmatites	Open pit, Podstepnoye, right bank	0.78	0.026	0.114	0.119	15.60	4.07	100	2560	3000	2720	2400	2700 ± 100
(3)	Monazite from Chudnov-Berdichev granitic rocks	Zhezhelev (open pit)	0.69	0.71	4.64	0.01	32.84	4.54	62.52	1980	2050	2120	2140	2100 ± 50
(4)	Zircon from charnockites	Sabarov, on South Bug River	0.028	0.055	0.054	0.21	65.27	10.11	24.11	1900	2050	1930	1860	1900 ± 50
(5)	Monazite from Kirovograd granites	Korotivograd, Sugakleya River	0.86	0.61	7.58	0.045	27.80	3.86	100	2000	1900	1920	1820	1950 ± 50
(6)	Monazite from black quartz granites	Checheliyevka, Ingulets River	0.4	0.22	4.45	0.02	16.79	2.29	100	2000	1670	1820	1620	2000 ± 100
(7)	Zircon from Rapakivi granites of Korosten complex	Korsun-Shevchenkivsky	0.017	0.035	0.02	0.57	56.66	13.74	29.03	1750	1590	1650	1700	1700 ± 50
(8)	Zircon from syenite, Priazov'ye alkali massif	Zhdanov, Priazov'ye (Azof coast)	0.011	0.004	0.07	0.67	23.13	11.63	100	1770	1830	1660	1880	1750 ± 100
(1)	Monazite from pegmatites cutting gneisses along White Sea	Alakurtti	0.30	0.12	2.45	0.02	15.52	2.03	100	1920	2040	2020	2200	1900 ± 100
(2)	Monazite from pegmatites cutting gneisses along White Sea	Lake Tedino	0.41	0.59	5.65	0.06	36.61	4.8	100	1860	1220	1440	1080	1900 ± 100
(3)	Zircon from Rapakivi granites	Viroyoki (Vyborg Rapakivi massif)	0.0114	0.0383	—	0.177	100	12.36	17.77	1640	1490	1558	—	1650 ± 50
(4)	Zircon from Rapakivi granites	Viroyoki (Vyborg Rapakivi massif)	0.005	0.0228	—	0.06	100	10.82	17.93	1650	1165	1350	1050	1650 ± 50

discovery of very ancient continental nuclei dated at more than 3000 m.y. in the central part of the Kola Peninsula and the Middle Dnieper Region (Ukraine).

Within the limits of the Ukrainian shield these strata, identified earlier as the so-called supercrystalline complex, were represented chiefly by xenoliths of gneisses and meta-amphibolites dated at more than 3000 m.y. found in the form of blocks among plagiogranites of granitized gneisses. The age of the latter, like that of numerous pegmatoid bodies that were intimately related in origin to the Dnieper migmatites, is dated at 2400 to 2800 m.y. The maximum age is undoubtedly more reliable, since it was obtained by both the Pb-U-Th and the ordinary lead methods.

TABLE 2  
AGES OF PRE-CAMBRIAN ROCKS OF THE UKRAINIAN SHIELD ACCORDING  
TO DATA OF THE K-AR METHOD

No.	Mineral and geologic description	Site	Age by K-Ar method (m.y.)	Probable age by U-Th-Pb method (m.y.)	References
(1)	Biotite from xenoliths of meta-amphibolite in plagiogranites	Taromsky open pit, Dnepr River	3050	2700	1
(2)	Biotite from medium-grained granodiorite-migmatite	Kaydaki station, open pit on Dnepr River	2820	2700	1
(3)	Muscovite from schists of Krivoy Rog stratum	Krivoy Rog	2100	2700-2100	1
(4)	Biotite from schists of Krivoy Rog stratum	Krivoy Rog	1900	2700-2100	1
(5)	Plagiogranite	Saksagan River	2100	2100	1
(6)	Biotite from Chudnov-Berdichev granites	Zhezhelev	1800	2100 $\pm$ 50	1
(7)	Biotite from charnockites	Sabarov, on South Bug River	1630	1900 $\pm$ 50	1
(8)	Biotite from Kirovograd granites	Kirovograd, Sugakleya River	1960	1950 $\pm$ 50	1
(9)	Biotite from Rapakivi granites	Korsun-Shevchenkovsky open pit	1715	1700 $\pm$ 50	1
(10)	Biotite from porphyritic granites	Uman, Staro-babansky open pit	1550		

The analogue of such relics of ancient rocks in the Baltic shield is a comparatively small ancient province in the northern part of the Kola Peninsula, established by the investigations of Polkanov and Gerling<sup>8</sup> in the area of the Voronezh River (TABLE 3). It is very interesting that a group of determinations of the isotopic composition of lead taken from ores at Monchegorsk gives a maximum Pb<sup>208</sup>-Pb<sup>204</sup> age of the same order. In light of this fact, the age of the Monchegorsk intrusion, which penetrates the Kola series of ancient gneisses and is considered to be Proterozoic on the basis of indirect geologic observations, is highly problematical. The age of 2500 m.y. obtained by the Ar-K method for the same gneisses in the area of Olenegorsk (which should be regarded only as an upper limit for metamorphism of these strata) allows us to conjecture that the entire suite of Kola gneisses stretching to the west will prove to be an ancient structure of the shield.



Apparently the gneisses of the White Sea formation are very close to this stratum in time, to judge from scattered age determinations on lead of galena from streaks cutting this formation on Medvezhy Island, calculated to be 3000 m.y. old (TABLE 5).

In individual parts of southern Karelia, outcrops of analogous ancient strata have been established (Suk-ozero), constituting the crystalline basement of the Karelian mountain chains.

TABLE 3  
AGES OF PRE-CAMBRIAN ROCKS OF THE BALTIC SHIELD,  
ACCORDING TO K-AR AND RB-SR METHODS<sup>8</sup>

No.	Description	Site	Age	
			by K-Ar	by Rb-Sr
(1)	Biotite from migmatites	Voron'ya River, Great Rapids	3440	
(2)	Biotite from migmatites	Voron'ya River, Great Rapids	3480	
(3)	Biotite from schists of Polmos suite	Leshaya	2660	
(4)	Muscovite from rare-metal pegmatites of Polmos suite	Vasin Myl'k	2340 $\pm$ 50	2600 $\pm$ 200
(5)	Muscovite from rare-metal pegmatites of Polmos suite	Polmos Tundra	2000 $\pm$ 50	2400 $\pm$ 180
(6)	Muscovite from spodumene pegmatites cutting Polmos suite	Lake Kolmozero	1740 $\pm$ 50	2380 $\pm$ 190
(7)	Muscovite from spodumene pegmatites cutting Polmos suite	Lake Kolmozero	2350	2270 $\pm$ 180
(8)	Biotite from biotite gneiss	Olenegorsk	2530	
(9)	Muscovite from pegmatites in gneiss-granites in pebbles of basal conglomerates of iron-ore formation	Sukozero	2540	
(10)	From pegmatites cutting gneisses along White Sea	Chupinsky district	1900	
(11)	Muscovite from pegmatites	Southern Karelia, Ulyalegi	2590	
(12)	Biotite from schist	Southern Karelia, Ulyalegi	1820	
(13)	Biotite from quartz-biotite-amphibolic schists of Parandovo series (pyritic formation)	Eastern Karelia, Parandovo	1760	
(14)	Biotite from Rapakivi granitic rocks	Vyborg	1620	1610 $\pm$ 40

However the lack of Pb-U-Th age determinations based on accessory minerals for these regions compels us to take a cautious attitude regarding the accuracy of dating of such very ancient blocks of rocks. It is very probable that their true age is even greater. This possibility has been adequately indicated by comparisons of Ar-K and Sr-Pb determinations for very ancient strata of the Kola Peninsula, which show that in the vast majority of instances the lack of agreement of ages is explained by a partial loss of argon and a resultant decrease in the ages obtained by the K-Ar method.

In the central part of the Russian Platform, in the crystalline basement of

TABLE 4

AGES OF PRE-CAMBRIAN ROCKS OF THE FUNDAMENT OF THE RUSSIAN PLATFORM

No.	Reference	Mineral and geologic description of rock	Site	Age by K-Ar (m.y.)
(1)	2	Biotite from gneisses of crystalline foundation of Voronezh block	Gubkin	2500
(2)	2	Biotite from schists of lower suite of Kursk metamorphosed series	Gubkin	2270
(3)	2	Plagioclase-microcline granite of penetrating strata of Kursk metamorphosed series	Gubkin	2050
(4)	2	Biotite from biotite porphyritic granite	Yakovlevo	1700
(5)	2	Biotite from biotite granite	Minsk	1630
(6)	2	Biotite from biotite granite	Gorky	1700
(7)	2	Biotite from biotite-plagioclase, granite-gneiss	Kaluga	1450
(8)	2	Biotite from microcline granite	Stalingrad	1450
(9)	2	Biotite-plagioclase, granite-gneiss	Ul'yanovsk	1250
(10)	2	Microcline granite	Mukhanovo	1320
(11)	2	Biotite-plagioclase, granite-gneiss	Glazovo	1350
(12)	2	Biotite from leucocratic granite	Nevel'	1340
(13)	7	Glaucinite from Ayzyan suite of Rhiphean	Western slope of Urals, Great Katav River	1260
(14)	7	Glaucinite from Lower Bavlinsky suite of Rhiphean	Volga-Uralian region, Serafimovskaya hole	1290
(15)	6	Biotite from granitic rocks of Berdyaush Plutonic formation	Central Urals, Berdyaush	1030
(16)	7	Glaucinite of Serdobsk series of Rhiphean	Serdobsk (depth 1790 m.), area of Pachelma depression	740
(17)	7	Glaucinite from laminarite layers	Serdobsk (depth 1380 m.), area of Pachelma depression	600

TABLE 5

AGES OF PRE-CAMBRIAN ORE OUTCROPS OF THE UKRAINIAN SHIELD BASED ON ORDINARY LEAD

No.	Reference	Site	Geological description of sample and deposit	Isotopic composition of lead			Age by		Assumed age (m.y.)
				Pb <sup>208</sup> /Pb <sup>204</sup>	Pb <sup>207</sup> /Pb <sup>204</sup>	Pb <sup>206</sup> /Pb <sup>204</sup>	Pb <sup>208</sup> /Pb <sup>204</sup>	Pb <sup>206</sup> /Pb <sup>204</sup>	
(1)	9	Veselyana, left bank of Middle Dnepr	Galena from quartz streaks in magnesite rocks. Magnetic anomaly	14.21	14.67	33.28	2630	2800	2700 ± 100
(2)	9	Krivoy Rog	Galena from sulfide streak in Lower Arkosic suite of Krivoy series	15.33	15.21	34.67	2100	2140	2100 ± 50
(3)	9	Krivoy Rog	Galena from streaks intersecting sodium metasomatites developing in rocks of Krivoy Rog stratum (mean of 4 determinations)	16.70	15.84	34.15	1380	880	900

TABLE 6  
AGES OF PRE-CAMBRIAN FORMATIONS AND ORE OUTCROPS OF BAL TIC SHIELD  
ACCORDING TO ORDINARY LEAD METHOD

No.	Reference	Site	Geological description of sample and site	Isotopic composition of lead			Age by		Assumed age (m.y.)
				Pb <sup>208</sup> /Pb <sup>204</sup>	Pb <sup>207</sup> /Pb <sup>204</sup>	Pb <sup>206</sup> /Pb <sup>204</sup>	Pb <sup>208</sup> /Pb <sup>204</sup>	Pb <sup>206</sup> /Pb <sup>204</sup>	
(1)	3	Monchegorsk ore field, Nittis-Kumuzh'ye	Massive magnetite ores from sulfide veins cutting Monchegorsk intrusion of basic composition penetrating Archean gneisses (Kola series)	13.64	14.56	32.24	2870	3300	3000 ± 300
(2)	3	Monchegorsk ore field, Nittis-Kumuzh'ye	Pyrrhotite from porphyritic formations of pentlandite (mean of 4 determinations)	14.30	14.74	33.66	2600	2620	3000 ± 300
(3)	3	Monchegorsk ore field, Nittis-Kumuzh'ye	Chalcopyrite-pyrrhotite ore (mean of 4 determinations)	14.29	14.79	33.59	2600	2650	3000 ± 300
(4)	3	Medvezhy Island, Kandalaksha Bay	Galena from quartz-carbonate veins in Archean gneisses (White Sea series)	14.04	14.65	32.87	2700	3000	3000 ± 300
(5)	3	Ulyalegi deposit, Southern Karelia	Pyrite-pyrrhotite ores from lenses in metamorphosed effusive-sedimentary formations analogous to Parandovsky series	14.07	14.59	33.08	2700	2870	2800 ± 100
(6)	3	Parandovo deposit, Eastern Karelia	Pyrite from pyritic lenses in strongly metamorphosed volcanogenic-sedimentary rocks of Parandovo series	14.27	14.91	33.75	2600	2570	2600 ± 100
(7)	3	Parandovo deposit, Eastern Karelia	Pyrite from pyritic lenses in strongly metamorphosed volcanogenic-sedimentary rocks of Parandovo series	14.39	14.89	33.88	2550	2500	2600 ± 100
(8)	3	Yalonvara deposit, Lake Ladoga area	Pyrrhotite from pyritic lenses in graphite schists and quartzites of Yalonvara series (analogue of Parandovo series)	15.48	15.11	34.29	2020	2300	2300 ± 100
(9)	3	Yalonvara deposit, Lake Ladoga area	Pyrite from the same location	15.43	15.05	34.28	2050	2300	2300 ± 100
(10)	3	Yalonvara deposit, Lake Ladoga area	Galena from quartz veins	14.90	15.02	34.24	2300	2320	2300 ± 100
(11)	3	Pitkyaranta deposit, Lake Ladoga area	Galena from streaks cutting magnetite ores of skarns lying at the base of the Ladoga formation	14.72	14.96	33.61	2400	2620	2700 ± 150
(12)	3	Pitkyaranta deposit, Lake Ladoga area	Galena from streaks cutting magnetite ores of skarns lying at the base of the Ladoga formation	14.26	14.77	33.23	2620	2800	2700 ± 150
(13)	5	Falun deposit, Sweden	Galena from ore-bearing skarn deposit in dolomites belonging to leptite formation	15.34	14.99	33.84	2100	2520	2520 ± 150
(14)	5	Orijarvi, Finland	Galena from polymetallic deposit in schists of leptite formation	15.74	15.46	34.08	1900	2360	2360 ± 150
(15)	4	White Sea area, pegmatites of northern veraki (?)	Galena from pegmatites penetrating White Sea stratum	14.58 14.97	14.80 19.13	35.20 35.00	2450 2280	1850 1950	1900 ± 50 1900 ± 50
(16)	4	White Sea area, pegmatites, Lake Tedino	Galena from pegmatites penetrating White Sea stratum	14.67	14.85	35.17	2420	1870	1900 ± 50

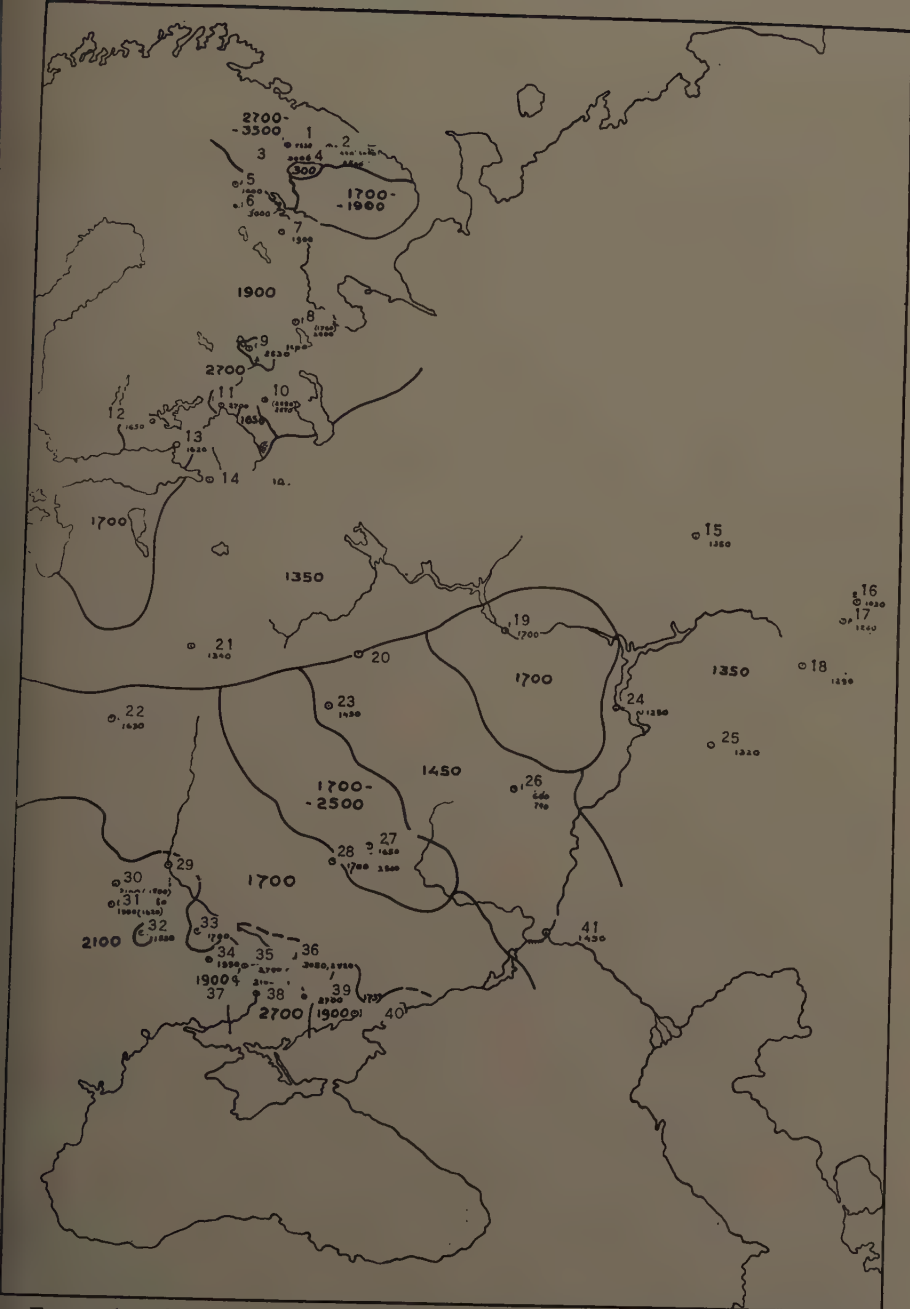


FIGURE 1. The age of Pre-Cambrian rocks of the Ukrainian and Baltic shields and the crystalline foundation of the Russian Platform. Ages given in millions of years. Locations: (1) Olenegorsk, 2530; (2) Voronja River, 3440 to 3480; (3) Monchegorsk, 3000; (4) Leshaya, 2660; (5) Alakurtti, 1900; Medvezhy Island, 3000; (7) Lake Tedino, 1900; (8) Parandovo, 1700; (9) Sukozero, 2530; (10) Ulyalegi (2590) 2870; (11) Pitkyaranta, 2700; (12) Viroyoki, 1650; (13) Vyborg, 1620; (14) Leningrad, 1320; (15) Glazovo, 1350; (16) Berdyash, 1030; (17) Great Katav River, 1260; (18) Serafimovskaya hole, 1290; (19) Gorky, 1700; (20) Moscow; (21) Nevel, 1340; (22) Minsk, 1630; (23) Kaluga, 1430; (24) Ulyanovsk, 1250; (25) Mukhanovo, 1320; (26) Serdobsk, 680, 740; (27) Gulkin, 1650, 2270, 2500; (28) Yakov-evo, 1700; (29) Kiev; (30) Zhezhelev, 2100 (1800); (31) Sabarovo, 1900 (1620); (32) Uman, 550; (33) Korsun, 1700; (34) Kirovograd, 1930; (35) Repyakhovka, 2700; (36) Dnepro-petrovsk, 3050, 2820; (37) Krivoy Rog, 2100; (38) Podstepnoye, 2700; (39) Veslyany, 2700; (40) Zhdanov, 1750; (41) Stalingrad, 1450.

the Voronezh massif, upon which lie the metamorphic rocks of the Kursk series with the iron-ore deposits of the Kursk magnetic anomaly (KMA) at their center, gneisses and schists dated at more than 2500 m.y. have also been found.

Thus, within the limits of the territory under consideration, at least three very ancient nuclei of Pre-Cambrian continents have been established.

The next age phase that is clearly differentiated within the Ukrainian and Baltic shields is an intense magmatism that encompassed practically the whole territory of both shields beginning 2100 m.y. ago, and ending about 1700 m.y. ago in the form of intrusions of the platform type, of alkali rocks, and of Rapakivi in the peripheral portions of both shields.

During the period that preceded this magmatism, the accumulation of the sediments of the Krivoy Rog series, the Kursk series of the KMA and, as will be shown, formed the metamorphic suites of the Karelids.

The earliest intrusions of this phase in the Ukrainian shield were the monazite-bearing granitic rocks of the Chudnov-Berdichev complex, the granodiorites of the Sob River to the southwest, and the plagiogranites of Kremenchug and Saksagan in the central areas of the shield.

Somewhat later came the complexes of the so-called Zhitomir and Kirovograd trachytic and black-quartz granites whose age fluctuates around 1900 m.y.

It is characteristic that, on the basis of two indices, the differences in ages given by different isotope ratios ( $Pb^{208}/Th^{232}$  and  $Pb^{207}/Pb^{206}$ ) and obtained by the Ar-K method within the Ukrainian shield, we can distinguish two great regions of intensive metamorphism of a very recent date: an area in the southwest part of the Ukrainian shield (the region of development of "Sobites" and of the charnockite formation) and the Ingulo-Saksagan watershed (the region of development of intrusions of the Tokovsky type). The lower age limit for this metamorphism is dated at 1500 to 1600 m.y. At the present time it is hard to establish the origin of this metamorphism or its true age with any reliability, so that it could equally well be an echo, as we will see below, of more recent magmatism of the same period within the Russian Platform or be connected, particularly in the southwest part of the Ukrainian shield, with Mesozoic vulcanism of the edge of the folded zone. In light of this fact we should note the appearance in the area of Uman of a granite massif with an age of 1600 m.y. A characteristic geochemical feature of almost all the granitic rocks of this cycle (except for the plagiogranites) is the fact that they contain monazites, which is not a characteristic of intrusions of the most recent period.

About 1700 m.y. ago in the area of Korosten (northwest) and Novo-Mirgorod (center) there appeared Rapakivi plutonic rocks and gabbro of the platform type and, in the Zhdanov area (southeast), there appeared alkaline intrusions of syenite composition.

This sort of detailed description of the intrusive cycles of the Ukraine has become possible only since the completion of almost a hundred age determinations by the Pb-U-Th method applied to accessory minerals. For this reason, a comparison of the magmatic history of the Ukrainian shield of this period with the Baltic shield and the Russian Platform is rather severely hampered by the absence of analogous detailed investigations by the Pb-U-Th method for these regions. However, on the basis of a large number of K-Ar determina-



tions in combination with individual determinations by the Pb-U-Th, we can nevertheless say that almost the entire territory of Karelia, Finland (Kuovo's data) and a considerable part of Sweden as well as the southeast part of the Kola peninsula were involved in intensive magmatism at this time.

It is a very responsible conclusion, drawn on the basis of recent age determinations, that the Svecofennide (Finno-Swedish) and Karelian mountain chains are of almost the same age.

We can estimate the time of sedimentation of these strata, subsequently transformed into intensively metamorphosed complexes, on the basis of the fact that the Lower Karelian (Parandovo and Gimol'skoye) iron-ore series are deposited on granite-gneisses showing ages of 2500 m.y. by the K-Ar method, while the post-Karelian intrusions are dated at 1850 to 1700 m.y., which coincides with the age of metamorphism of the metamorphic karelide strata themselves (based on the K-Ar method).

On the basis of the isotopic composition of ordinary lead taken from sulfide ores of volcanogenic and sedimentary rocks of the Parandovo series and its analogues, as well as those of the leptite formation of Sweden and Finland, the time of sedimentation of these strata is dated at 2800 to 2300 m.y. on the basis of  $Pb^{208}/Pb^{204}$ , which roughly coincides with the preceding data if we take into account the fact that the K-Ar method for gneisses can give only an upper limit for the age of sedimentation of the primary substance of which they are composed.

Thus, the time of accumulation of iron-ore formations in the Pre-Cambrian of the Baltic shield, the Voronezh massif (Kursk series), and the Ukrainian shield (Krivoy Rog series) is actually identical and covers the interval from 2700 to 2100 m.y.

In the contrast to the Ukrainian shield, within the southeast part of the Baltic shield the most recent post-Karelian magmatism had a much more extensive development, having been characterized by a widespread intrusion of Rapakivi plutonic rocks about 1600 m.y. ago. All these data convincingly indicate the very ancient character of both shields, within which magmatic activity ended 1700 to 1600 m.y. years ago, if we omit the plutonic rocks of platform type that appeared during the Paleozoic in the north of the Baltic shield (the Khibiny Mountains).

This brings us to the natural question of the character of the geological history of the whole Russian Platform during the period between this date (1600 m.y.) and the Cambrian (600 m.y.). Was the platform an ancient structure like the African continent that left traces of very recent Pre-Cambrian tectonic movements and magmatism, or did its geologic development, like that of the two shields it contains, actually end 1600 m.y. ago?

A partial answer to this question has been given by investigations of the crystalline foundation of the Russian Platform based on core samples from deep holes produced by supportive drilling.<sup>2</sup>

It has been found that, except for the comparatively small Voronezh massif, almost the entire territory of the foundation was involved in intensive magmatism 1700 to 1600 m.y. years ago, and later than 1450 to 1350 m.y. years ago. During this period connected with the establishment of the outlying Rapakivi plutonic rocks in the peripheral portions of shields consolidated earlier,

the center of magmatic activity largely moved to the Russian Platform, or in any case remained only within its limits—which is more probable—since we have no proof of the absence of more ancient magmatism within its limits.

It is characteristic that these younger zones of magmatism stretch to the northwest, spatially coinciding with areas of later depressions and with the accumulation of very thick sedimentary deposits after the Pre-Cambrian and Paleozoic periods (Dnieper and Pachelma depressions).

Thus this part of the Russian Platform in its present-day state structurally reflects, so to speak, the initial stage in the development of the shield, a stage characterized by differential movements of individual blocks connected with incomplete consolidation of Pre-Cambrian folded zones. In contrast to it, the Baltic and Ukrainian shields are characterized by permanent epeirogenic movements of a positive sign and of equal amplitudes for the various parts, which gives evidence of a sudden elevation of whole blocks accompanied by intensive denudation. It is precisely this fact that explains the rectilinear boundaries of the shields and the large tectonic dislocations along them, whereas it is characteristic for the border regions of the platform with their folded zones to display advance depressions and smoother transitions from one structure to the next.

An essential feature of the platform in addition to this, a consequence of its differential vertical movements, is its thick cover of sedimentary strata of Pre-Cambrian and Paleomesozoic origin. As measurements of the ages of glauconites by the K-Ar method performed by Plevaya and Kazakov have shown,<sup>7</sup> the most ancient suites of this cover—the Lower Bavlinskaya and the Avzyanskaya—are no older than 1300 m.y. Only the effusive rocks of the Ovruchskaya series found in the northwest part of the Ukrainian shield belong to somewhat older formations, having an age of about 1400 m.y., conditionally assigned to the Jotnian. At the same time our measurements of the age of individual granitic rocks on the eastern side of the platform, similar to the measurements of the age of the Berdyaushsky plutonic rocks and the Shingersky massif in the Urals that intersect the Lower Bavlinsky suite (according to the data of Ovchinnikov and Garriss),<sup>6</sup> showed ages of 1030 to 1220 m.y. Thus, in the course of formation of the Pre-Cambrian sedimentary cover of the platform spanning a period of at least 700 m.y., there occurred still another great tectonic-magmatic cycle in the eastern part of the platform. The intrusions of this cycle apparently were synchronous with the well-known pegmatoid formations of southern Scandinavia (Arendal *et al.*), giving evidence of definite foci of magmatism that developed around the periphery of the platform during this period.

Everything we have said above enables us to depict the following sequence of geological events in the Pre-Cambrian of the territory in question:

The formation of the Pre-Cambrian continent that consisted of the Ukrainian and Baltic shields and the crystalline foundation of the Russian Platform connecting them took place over a long period of time, beginning at least 3600 m.y. ago. Approximately  $1900 \pm 100$  m.y. ago, the consolidation of the Ukrainian and Baltic shields was completed. The Rapakivi plutonic formations and alkaline intrusions that developed somewhat later (1700 to 1600 m.y. ago) along the edges of these shields bordering the Russian Platform were

only a repercussion of the intensive magmatism that involved the entire territory of the platform, of which only a small area—consolidated earlier—in the form of the Voronezh massif remained firm during this period.

The rest of the geologic history of the continent has proceeded under the influence of a gradual decrease in the intensity of magmatism and migration of this magmatism into the region of the younger folded zones around the periphery of the platform.

The differential vertical movements of individual blocks of the platform, which have caused the accumulation of thick strata of sedimentary cover of late Pre-Cambrian and Paleomesozoic age in the region of the lowest depressions coinciding with the zones of the most recent Pre-Cambrian magmatism, indicate that the process of transformation of the platform into the monolithic structure of a shield was not completed.

The picture that has evolved of the sequence of geologic events in the Pre-Cambrian history of the Ukrainian and Baltic shields and the foundation of the Russian Platform is striking in its obvious similarity to the histories of other Pre-Cambrian continents of the planet. For this reason we consider it reasonable to suggest the following rough subdivision of the Pre-Cambrian

TABLE 7  
SCHEME OF SUBDIVISION OF PRE-CAMBRIAN

Boundaries (m.y.)	Name of era
600 $\pm$ 50	Upper Proterozoic
1100 $\pm$ 100	Lower Proterozoic
1900 $\pm$ 100	Archean
2700 $\pm$ 150	Katarchean
3600 $\pm$ 200	(?)

into four main eras, clearly differentiated in the European Pre-Cambrian and probably characteristic of the Pre-Cambrian throughout the world (TABLE 7).

The reason for this sort of division is the special significance of the boundary 1900  $\pm$  100 m.y. in the history of the earth, after which the scales of magmatism and metamorphism lessened greatly in intensity and the lithology of sediments changed sharply in the direction of a marked predominance of organogenic material in sedimentation. It is highly probable that this important turning point in the history of the earth coincides with the period of marked reduction in the amount of radioactive heat in the earth's crust as a result of the substantial decay of the radioactive elements (the principal energy radiators)  $K^{40}$  and  $U^{235}$ .

In the light of this it is logical to recognize this critical moment in the history of the earth, previously known as the White Sea epoch of magmatism, as the boundary between the Archean and the Proterozoic.

The planetary character of the tectonic-magmatic epoch corresponding to the Grenville epoch of magmatism (110  $\pm$  100 m.y. ago) enables us to subdivide the Proterozoic into two independent eras: the Upper and Lower Proterozoic. It is suggested that the terms Rhiphean, which has been adopted for designating sediments of this age in the U.S.S.R., or Sinian in the Chinese People's Republic be given local significance.

For the most ancient nuclei of the Pre-Cambrian continents of the earth's crust, whose origin approaches the hypothetical time of formation of the planet itself, it is useful to adopt the name suggested by A. A. Polkanov: Katararchean.

### *Summary*

Investigation of the geological age of Pre-Cambrian rocks of the Ukrainian and Baltic shields makes it possible to establish the synchronicity of great geological events comparable in their intensity and their metallogenetic specificity.

The formation of both shields took place during a long period of geological time, from 3500 to 1900 m.y. ago. The most intensive periods of magmatism were  $3200 \pm 300$ ,  $2600 \pm 200$  and  $1900 \pm 100$  m.y. This confirms the existence of great megacycles in the geological history of the earth's crust with the period of renewal every 600 m.y.

The most ancient rocks in the European Pre-Cambrian (that is, Katararchean blocks of gneisses and migmatites) have been discovered on the north shore of the Kola Peninsula and in the middle Dnepro region ( $3200 \pm 300$  m.y.).

The rocks  $2600 \pm 200$  m.y. of age are granite-gneisses and migmatites of the Dnepro region and the Ladoga formations.

The epoch of  $1900 \pm 100$  m.y. was distinguished by the greatest magmatic activity in the whole Pre-Cambrian. In this epoch the main granitoid massifs of the Ukraine and the Svecofennidic and Karelidic orogens of the Baltic shield appeared.

In the period 2600-1900 m.y. the sediments of the Krivoi Rog type were accumulated within the limits of both shields.

Magmatic activity migrated to the territory of the modern Russian Platform 1700-1400 m.y. ago. Among the crystalline rocks of the basement of the Russian Platform we now find the remains of the most ancient rocks and structures (Woronezhsky Massif, 2500 m.y.). The submeridional stretches of the structures, which are typical for the ancient blocks, were replaced at this time into the sublatitudinal ones. For example, the beginning of this period is characterized by the appearance of Rapakivi intrusions, typical platform plutons, that surround the Ukrainian shield from the north and the Baltic shield from the south.

Later, beginning about 1400 m.y. ago, the information of the sediment cover of the Russian Platform began; it has been finished only in modern time after the deposition of the Paleozoic, Mesozoic, and Cenozoic sediments of great thickness.

These weakly metamorphosed, upper Pre-Cambrian sediments of very large thickness accumulated particularly in downwarps of the crystalline basement. It is interesting to note that these structural basins coincided with the regions of magmatic activity that occurred approximately 100 m.y. before (that is, at 1600 to 1400 m.y.). A good example is seen in the territory of the Pachelm basin.

The Pre-Cambrian cover of the crystalline basement of the Russian Platform may be divided into three divisions of different geological age: (1) Iotny (Shokshinsky sandstones, effusive rocks of Ovrutch series and others, 1400 to



1300 m.y.); (2) lower Rifei (Giperborei sandstones from Kildin Peninsula, sediments of the Low-Bavlinkaja series in the Ural and others, 1300 to 1100 m.y.); and (3) upper Rifei (sandstones and argillites of Karataush series in the Ural, Serdob series of the Patchelm basin and others, 1100 to 600 m.y.).

On the border between Lower and Upper Rifei in the eastern part of the Russian Platform on the territory of the Volga-Ural depression, a weak magmatic activity took place (diabase-dikes, Rapakivi intrusion of Berdiaush).

While the formation of the Ukrainian and the Baltic shields ended approximately about 1900 to 1700 m.y. ago, the magmatic activity on the territory of the Russian Platform continued until 1000 m.y. ago. The vertical movements of some Pre-Cambrian blocks consolidated somewhat later than the crystalline basement of the Russian Platform can be observed at the present time.

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## Part VI. The Age of the Basement Rocks of the World: Africa and Australia

### RADIOACTIVE AGES FROM THE PRE-CAMBRIAN ROCKS OF AUSTRALIA

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In this review most of the Australian rock ages that have been determined by radioactive methods are discussed. The Australian National University, Canberra, and the University of Western Australia, Perth, are the only two organizations in Australia at present carrying out isotopic measurements related to geochronological problems. All the previously unpublished ages contained in this paper were determined at the University of Western Australia.

Before discussing the various isotopic ages that have been measured so far it is relevant to mention briefly the accuracy associated with the new data presented here so that world-wide age correlations can be made.

#### *Absolute Accuracy*

The U-Pb determinations of Greenhalgh and Jeffery,<sup>1</sup> were made using normal chemical techniques combined with an isotopic analysis of the lead as a lead tetramethyl. Although standard lead samples obtained from J. T. Wilson of the University of Toronto in Canada were used to check memory effects and mass discrimination during mass spectrometry, there is still a possibility that some of these determinations suffered from a slight memory effect. Such an effect, if present, was certainly small. Reasonable agreement between the Rb-Sr, K-Ar, and U-Pb ages of cogenetic minerals has been obtained in some localities (FIGURE 1; TABLE 1, No. 39).

All Rb-Sr ages have been calculated from data obtained by isotope dilution and standardized by gravimetric determinations of pure rubidium and strontium salts and by comparisons with the results of Jeffery<sup>2</sup> and Compston<sup>3</sup> carried out at the Carnegie Institution of Washington, Department of Terrestrial Magnetism, Washington, D.C.

Potassium was determined by flame photometry using N.B.S. feldspar number 70 as a standard. The isotope-dilution method with A<sup>38</sup> as a tracer was used to find the amount of radiogenic A<sup>40</sup> in samples.

We believe that a conservative estimate of the total absolute errors in the ages measured at the University of Western Australia due to the physical measurements are: U-Pb,  $\pm 4$  per cent (assuming no common lead); Rb-Sr,  $\pm 3$  per cent; and K-Ar,  $\pm 5$  per cent.

From the geochemical point of view probably the most accurately dated area in Australia is at Boya near Perth, where the total-rock method of dating granites<sup>4</sup> has yielded an absolute granite age of emplacement of 2700 million years (m.y.).

*Australian Pre-Cambrian Ages\**

*The 2700-m.y. nucleus.* TABLE 1 and FIGURE 1 contain most of the information that is at present available concerning isotopic ages in Australia. Ages determined as part of the Australian Bureau of Mineral Resources age program have not been included as they will be discussed elsewhere.

The oldest rocks dated thus far are all located in Western Australia, where an age of about 2700 m.y. has been measured in a number of different localities.

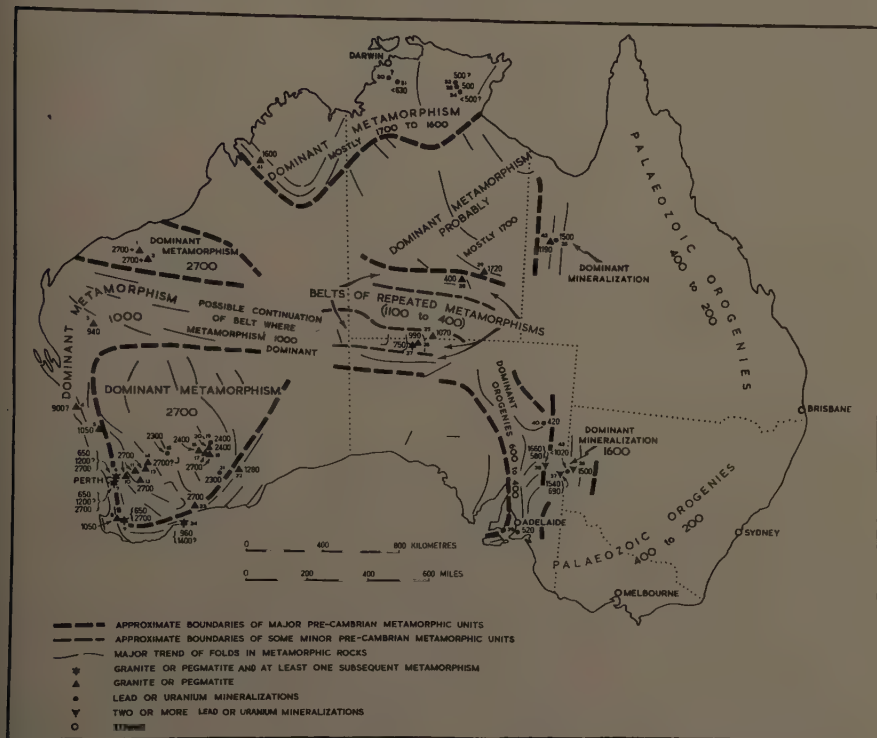


FIGURE 1. Numbers 1 to 43 refer to localities in TABLE 1, other numbers (for example, 2700) refer to age in millions of years.

It has become clear that the main Pre-Cambrian 2700-m.y. nucleus extends from Pilbara Province in the northwest almost to the south coast, being cut between the Pilbara and the Kalgoorlie-York Province by unaltered Proterozoic sediments in which pegmatitic muscovite has given an age of 940 m.y. (3).

There is a possibility that the ages determined in the Pilbara Province (1 and 2) represent a real age that is slightly greater than 2700 m.y., but this has not been proved. These ages were all determined on pegmatitic minerals that were intrusive into the country rock, the Warrawoona older "greenstone" series. Greenstones, the oldest known rocks in Australia on structural evi-

\* Numbers in boldface, for example 3, refer to specific localities indicated in FIGURE 1.

TABLE 1

Map No.	Locality	Mineral*	Inferred age			
			Rb-Sr**	K-Ar†	U-Pb‡ or common lead	Reference
1	Wodgina	Muscovite (p)	2940	2300	~2500	2
		Feldspar (p)	2850	2070		2
2	Woodstock	Tanteuxenite				1
3	Yinnietharra	Muscovite (p)	940	890		3
4	Mullinyu	Muscovite (p)	900 (?)			3
5	Yandanooka	Muscovite (p)	1050			3
6	Mundaring	Granite	2700		2335	4
		Muscovite (p)	2700			4
		Epidote (g)	1200 (?)			4
		Biotite (g,p)	650			4
7	Boya	Granite	2700			4
		Biotite (g)	650			4
		Epidote (g)	1200			5
8	Mullalyup	Muscovite (p)	1050			5
9	Hester	Granite	2660			5
		Biotite (g)	650			5
10	York	Muscovite (p)	2700			5
11	Cunderdin	Biotite (g)	2600	2600		5
12	S. Quairading	Muscovite (p)	2700			5
13	Doodlakine	Granite	2750		2405	5
		Biotite (g)	2610			5
14	N. Hines Hill	Biotite (p)		2540		5
		Biotite (p)	2480	2560		5
15	Bullfinch	Galena				8
16	Bullabulling	Biotite (p)	2400			8
17	Grosmont	Lepidolite (p)	2640	2670		2
		Feldspar (p)	2740	2630		2
18	Londonderry	Muscovite (p)	3200	2590		2
		Feldspar (p)	2760	2090		2
19	Kalgoorlie	Galena				8
20	Mungari	Muscovite (g)	2400			8
21	Norseman	Galena				8
22	Fraser Range	Muscovite (p)	1280	1210		3
23	Ravensthorpe	Muscovite (g)	2810	2700		2
		Feldspar (p)	2710	2070		2
24	Doubtful Island Bay	Allanite			1400 (?)	5
		Biotite (p)	960			5
25	Kulgera	Muscovite (p)	1070			5
26	Sentinel Hill	Muscovite (p)		990		5
27	Ernabella	Biotite (p)	750			5
28	Hart Range	Samarskite				5
		Muscovite (p)	410	370		1
29	Grant Bluff	Biotite (g)	1720			5

\* Absite (thorian brannerite); granite is total-rock measurement; galena is Pb = Pb age only; (p) is pegmatite; (g) is granite.

\*\* Rb<sup>87</sup> → Sr<sup>87</sup>;  $\lambda = 1.386 \times 10^{-11}$ /year; 6, 7, and 9, Rb-Sr age on granite calculated by total-rock method,<sup>4</sup> biotite, muscovite, and epidote ages are values when Sr(87/86) of granite and mineral were the same; 13 is granite age calculated using Sr(87/86) = 0.70, and biotite age value when Sr(87/86) of granite and biotite were the same; 29 is age value when Sr(87/86) of granite and biotite were the same.

† K<sup>40</sup> → Ar<sup>40</sup>;  $\lambda = 5.303 \times 10^{-10}$ /year, R = 0.124.

‡ U<sup>238</sup>;  $\lambda = 1.541 \times 10^{-10}$ /year; U<sup>235</sup>;  $\lambda = 9.722 \times 10^{-10}$ /year; Th<sup>232</sup>;  $\lambda = 4.987 \times 10^{-11}$ /year. (Greenhalgh and Jeffery.<sup>4</sup>) Most probable age is given in cases of discordancy. Map Nos. 24, nonisotopic age with probably large, unknown error; 30, ages very discordant.

§ Unpublished ages measured at University of Western Australia.

TABLE 1—*Continued*

Map No.	Locality	Mineral*	Inferred age			
			Rb-Sr**	K-Ar†	U-Pb‡ or common lead	Refer- ence
30	Adelaide River	Uraninite			Proterozoic	1
31	Brock's Creek	Uraninite			<630	1
32	El Sharana	Uraninite			500(?)	1
33	Palette	Uraninite			500	1
34	Sleisbeck	Uraninite			<500(?)	1
35	Mt. Isa	Galena			1500	9
36	Broken Hill	Galena			1500	9
37	Radium Hill	Davidite			1540	10
		Davidite			690	1
38	Crocker's Well	Absite			580	11
		Absite			670	1
		Biotite (p)		560		§
		Davidite			1660	1
39	Myponga	Uraninite			520	1
		Biotite (p)		565		§
		Biotite (p)	510			§
40	Mt. Painter	Samarskite			420	12
41	Leopold Range	Muscovite (p)	1600(?)			§
42	Mt. Isa (west)	Monazite			1190	13
43	Baker's Prospect	Galena			1020	9

dence, are dominantly basaltic and andesitic lavas. These rocks extend through the Kalgoorlie System and are the principal host rocks of gold in Western Australia. In the Kalgoorlie region the age of the closing phase of the original metamorphism of the greenstones is 2700 m.y., dated from pegmatitic intrusions at Londonderry (18) and Grosmont (17). Elsewhere in the gold fields (15, 19, and 21), galena from the gold lodes gives ages from 2300 to 2400 m.y. The Mungari granite (20) is the nearest granite to the Kalgoorlie lodes and has an age of 2400 m.y., identical with that at Bullabulling (16). Thus it is clear that there were two major periods of granite injection in this area.

The granites to the west of the gold fields have been measured as 2700 m.y. old and inject and granitize a gneissic complex, among which are charnockitic rocks of all types. Some of the "remetamorphosed" gneisses may represent the original basement rocks<sup>5</sup> in this vicinity, and attempts to discover ages greater than 2700 m.y. are in progress. No evidence of the 2400-m.y. metamorphism has been found thus far outside the gold-fields area. The western margin of the central nucleus, having as its most striking feature the Darling Scarp near Perth, separates the granitic rocks of the Shield from more than 30,000 to 40,000 feet of post-Pre-Cambrian sediments and metamorphic rocks. In several places (4, 5, and 8) intrusives into these rocks have been dated and indicate that a major phase of granite and pegmatite activity took place about 1000 m.y. ago.

In the Archean granites near Perth (6 and 7) there is some indication of a 1200-m.y. metamorphism and good evidence of a pronounced metamorphism at 650 m.y. Acid igneous activity did not take place at this time, but there

was abundant injection of quartz dolerite dikes both at locations **6** and **7** near Perth and farther south at **9**, where Archean granite has again revealed the 650-m.-y. metamorphism. Granitic rocks (**10** and **14**), a few miles to the east of **9**, show no sign of superimposed metamorphism of this type.

The southern margin of the nucleus appears to be bounded by an area of high-grade gneisses and granulites together with charnockitic rocks that are cut by allanite-bearing pegmatites. Few age determinations have been made in this area, but a biotite age of 960 m.y. (**24**), a doubtful allanite age of 1400 m.y., and the general lithological character of the country rocks all suggest that this southern margin is similar in age to the zone adjoining the southeastern-trending boundary of the nucleus dated at 1280 m.y. (**22**). The Fraser Range in which **22** occurs is separated from the main Kalgoorlie-York nucleus by the Fraser Fault, and it seems reasonable to associate the 1280-m.-y. event with the waning phase of the major movements of the fault and the metamorphism that produced the charnockitic rocks.

#### *Northern Australia*

In this region pegmatitic muscovite in the Leopold Ranges at **41** has an age of about 1600 m.y., and it is tentatively suggested that it was formed during the granite injection into the main metamorphic rocks of the northern part of the Northern Territory, the Brocks Creek Group, since K-Ar ages on granitic biotite have ranged from 1500 to 1700 m.y.<sup>6</sup>

In the country rock the ages of uraninite mineralization have been shown to be 500 m.y. at El Sharana (**32**) and the Palette Lode (**33**), with a slightly younger age at Sleisbeck (**34**) and completely discordant ages at Adelaide River (**30**).

It is concluded that near the beginning of the Paleozoic a mild metamorphism affected this area, and that at this time the uranium mineralization took place.

#### *Central Australia*

The oldest rocks in central Australia are in the Arunta Complex, and these can be shown on stratigraphic grounds to be of early Pre-Cambrian age. However no isotopic ages thus far have indicated this extreme age. Several ages have been determined on muscovite and samarskites from coarse pegmatites in the Hart Range (**28**), which give an age close to 400 m.y. At the present stage of knowledge it is assumed that during the time that the Adelaide System several hundred miles to the south was being metamorphosed there was sufficient metamorphic activity in the Hart Range to produce Paleozoic mica pegmatites that cut the Archean basement. Throughout the Hart Range area repeated metamorphisms, hitherto presumed to have taken place in Archean times, are in evidence. All isotopic ages available for this region, unfortunately, have been made on pegmatites related to some of the latest acidic intrusions. This problem is being investigated further to establish the absolute age of the Arunta Complex.

To the northeast of the Hart Range, biotite from the granitic rocks at Grant Bluff (**29**) are about 1720 m.y. old by Rb-Sr measurements.



*South of the Amadeus Trough*

The Amadeus Trough lies to the north of the Musgrave Province, and in this region upper Proterozoic and lower Paleozoic sediments prevail. The Musgrave block itself has suffered a complex series of igneous phenomena, most of which are presumed to have taken place in Archean times. An Rb-Sr age from Kulgera (25) gave 1070 m.y. for a pegmatite muscovite, while in the eastern Musgraves at Sentinel Hill (26) the age is 990 m.y. by the K-Ar method. From these measurements it is suggested that a major phase of granite formation took place about 1000 m.y. ago with some later metamorphism at 750 m.y. (27). The pegmatization at Yinnetharra (3) and along the west coast (4, 5, and 8) may well be related to the igneous activity of the Musgrave block since the ages and tectonics of these areas are rather similar.

*South Australia and Broken Hill Region of New South Wales*

The uranium deposits at Radium Hill (37) and Crocker Well (38) have been shown to be situated in country rocks between 1500 and 1700 m.y. old, while the mineralization itself seems to have occurred about 600 to 700 m.y. ago. The mineralization at these two localities is thought to be due to the breakup of the great geosyncline in which the sediments of the Adelaide System were laid down. Under such conditions we should expect the basement rocks of the geosyncline to fracture and become remineralized. Similar young ages have been found at Mt. Painter (40) and at Myponga (39). The paucity of age data is a severe handicap to the interpretation of the Pre-Cambrian sequence in this part of Australia.

*Mt. Isa Region*

Galena from the Mt. Isa lead and copper fields of north Queensland (35) has been shown by Stanton and Russell<sup>7</sup> to have an isotopic composition very similar to the galena at Broken Hill. It may be assumed on this evidence that their ages (1500 m.y.) are the same.

An approximate monazite age of 1190 m.y. (42) is associated with the nearest granites to the west of the Mt. Isa Mines.

*Conclusions*

Sufficient isotopic ages have been measured to suggest a basic subdivision of the Australian Pre-Cambrian basement rocks. The oldest province occurs in Western Australia where huge tracts of granitic rocks are about 2700 m.y. old and are flanked and dissected by orogenic belts of much younger rocks.

On the eastern side of the chief 2700-m.-y. nucleus there is evidence of a strong metamorphism that occurred about 2300 to 2400 m.y. ago. This event was probably responsible for the production of gold ores and granite injection in the Kalgoorlie-Norseman region.

The entire nucleus is enclosed on three sides by younger rocks that were extensively pegmatized between 1000 and 1300 m.y. ago.

In northern Australia major orogenic activity between 1000 and 1700 m.y. ago is in evidence over a large area of country. The uranium mineralization here appears to have occurred approximately 500 m.y. ago. Ages in the Willy-

ama Province at Mt. Isa and in the Davenport Province seem to fall in the range of 1500 to 1600 m.y.

There is a strong suggestion that the ages of 900 to 1100 m.y. found in the Musgrave Ranges probably date an east-west belt of activity that continues through to the west coast and defines a minimum age for the deposition of the Proterozoic sediments separating the Pilbara and Kalgoorlie-York Provinces.

The orogenic activity related to the Adelaide geosyncline in south Australia extended far to the north into central Australia. Throughout this extensive area metamorphic activity and mineralization ranges from 400 to 600 m.y. and in several places can be found superimposed on much older rocks.

On the eastern side of Australia no isotopic age data are available, and the main orogenic activity appears to be associated with the breakup of the Tasman geosyncline about 400 to 200 m.y. ago.

The division into provinces and the extrapolations discussed in this paper should be considered as only tentative. More ages, together with detailed investigations of critical areas, will be required before these suggestions can be confirmed.

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# SUMMARY OF DISCUSSION OF GEOCHRONOLOGY OF PROTEROZOIC GRANITES IN NORTHERN TERRITORY, AUSTRALIA

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Two recent investigations\* by P. M. Hurley, N. H. Fisher, W. H. Pinson, B. P. Walpole, K. G. Smith, and H. W. Fairbairn present K-Ar age analyses of 24 Proterozoic granites from the Northern Territory of Australia. These show two chief groups of ages averaging 1650 and 1440 million years (m.y.). Both groups of granite were emplaced at the end of a period of folding. The regional structure connects the first period of folding with the lower and the second with the upper subdivision of what is regarded as the Lower Proterozoic, so that the intrusion of the older group of granites (1650 m.y.) marks the end of the lower subdivision and the younger group (1440 m.y.) the close of Lower Proterozoic time and the beginning of Upper Proterozoic. The base of the Proterozoic would naturally be older than 1650 m.y.

Rubidium-strontium measurements on a sample from each of these groups give results in agreement with the above.

## *Discussion of the Papers*

R. D. RUSSELL (*University of British Columbia, Vancouver, B. C., Canada*): In looking at common lead isotope abundances, we are seeing the superposition of a number of effects, and in any particular instance the interpretation may be difficult. At the same time the individual effects are rather simple in themselves, so there is some hope of understanding them.

Therefore I do not think it is safe to adopt a general formula of dating galenas on a routine basis. However I do believe that useful age information can be gained as a by-product of lead-isotope studies and, furthermore, that there will be special cases in the future when rather precise age information can be obtained in this way.

Ron Farquhar and I have tried to sort out some families of galenas that seem to show rather simple relationships in the hope that we could understand these.

In this regard, we looked at suites from Mount Isa, Queensland, and Broken Hill, New South Wales in Australia. These results, which have been published in the literature,<sup>4</sup> show a conformable layer at Broken Hill having substantially constant isotopic composition and another conformable layer at Mount Isa with similarly constant isotopic composition.

More recently, at the University of British Columbia, we have been concentrating on refinement of our measurements. Quite recently, within the past few weeks, we have been doing some work with a new mass spectrometer, involving the comparison of lead tetramethyl samples with a standard. We can do this rather quickly now, and we have improved our precision to the point that, when we plot the points representing these conformable layers, we

\* To be published in the *Bulletin of the Geological Society of America*.

get a cluster with about the same centers, but the dimensions of the cluster are reduced nearly tenfold.

We can say now that, for the conformable layer at Broken Hill, the extreme  $Pb^{204}$  values measured thus far (about one-half dozen analyses) do not differ by more than 0.15 per cent.

We think we have now measured a significant difference between Mount Isa and Broken Hill. The Mount Isa samples differ in isotope ratios from the Broken Hill sample by less than 0.5 per cent in any ratio, which again bears out the fact that these are remarkably similar.

Now unless this is a rather remarkable coincidence, the similarity in isotopic composition suggests that these two deposits may have been derived from a common source at slightly different times and, no matter what model is accepted, the time interval becomes very small, approximately 40 m.y.

To go on to more dangerous ground, Stanton<sup>5,6</sup> suggested that the conformable layer at both of these places was laid down off volcanic island arcs. This hypothesis suggests the possibility of an arc through Western Australia with an age of about 1600 m.y.

I stress that this is very new work<sup>7</sup> and that these are preliminary measurements; we have no desire to put too much emphasis on this interpretation.

At Toronto we did work on Thackaringa-type deposits at Broken Hill that contain anomalous lead. A report on this work has been published, so I shall not dwell on it, but we put an upper limit to the time of last alteration of these leads, which was, as I remember, significantly younger than the age we postulated for the conformable layer ( $1020 \pm 150$  m.y.).

L. O. NICOLAYSEN (*Bernard Price Institute of Geophysical Research, Johannesburg, Union of South Africa*): Last year there were two important communications from the South Australian Museum about fossils in the Ediacara quartzites 280 miles north of Adelaide.<sup>1,2</sup> The Ediacara fauna occurs about 200 ft. below material known to be Lower Cambrian (*Archeocyatha*, *Brachiopods*); it is unlike any Lower Cambrian fauna and is assigned by Glaessner to the late Pre-Cambrian. It includes the genus *Rangea*, described about 30 years ago<sup>3</sup> from the Nama system in South-West Africa; this is a flat-lying succession of sedimentary rocks. There may develop a need for a new system deserving a world-wide name and systematic status. I suggest that any age measurements that can assign definite limits to the time of deposition of the Ediacara quartzites might be extremely valuable. We shall try to complement such work with further data on the Nama system of South-West Africa. All that we have established thus far is that it has an age  $<950 \pm 50$  m.y.

R. W. FAIRBRIDGE (*Columbia University, New York, N. Y.*): As regards a systemic name, there is one in the literature called the Adelaide system, which includes the *Ediatia* quartzites. This name is quite well recognized. That system, incidentally, can be followed stratigraphically up into that area of intense confusion in central Australia where the only dates are about 1400 m.y., which, of course, are quite unsatisfactory. These dates are in the Pre-Cambrian but quite clearly in what we used to call Proterozoic.

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## AN UPPER LIMIT TO THE AGE OF THE WITWATERSRAND SYSTEM

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In the Central Rand area near Johannesburg the Witwatersrand System lies directly on the Old Granite. On the West Rand the Dominion Reef System, consisting chiefly of rhyolitic and andesitic lavas, lies between the Witwatersrand System and the Old Granite. G. D. L. Schreiner (personal communication) made measurements on rhyolitic lavas collected at the surface and on a sample of granite from a borehole core that passed through the lavas into the Old Granite. While this work was in progress H. L. Allsopp collected and measured samples from the Old Granite exposure to the north of Johannesburg.

### *Measurements on the Old Granite*

Measurements have been made on four samples of the "total rock" on separated mineral fractions from one of these samples and on feldspar and biotite from pegmatites in the area. All the measurements at present available are given in FIGURE 1, which is a plot of  $\text{Sr}^{87}/\text{Sr}^{86}$  (number of atoms) against  $\text{Rb}^{87}/\text{Sr}^{86}$  (by weight) on two scales. The two scales are necessary because of the wide range of values of  $\text{Rb}^{87}/\text{Sr}^{86}$ , 1 to 600, covered by these measurements. It will be noted that the total rock measurements in FIGURE 1b lie very close to a straight line and imply an *ab initio* value for the ratio  $\text{Sr}^{87}/\text{Sr}^{86}$  of about 0.716. The age of the rock is equal to  $T_{1/2} \ln[1 + (87/86) \times \text{slope of plot}] / \ln 2$ . From the measured slope the age is found to be 3100 million years ( $\lambda \text{Rb} = 1.39 \times 10^{-11} \text{ years}^{-1}$ ). Fuller details of the measurements will be published elsewhere by H. L. Allsopp of this institute.

Compston and Jeffery use a plot of  $\text{Rb}^{87}/\text{Sr}^{87}$  against the *ab initio* value of the ratio  $\text{Sr}^{87}/\text{Sr}^{86}$ . Points on the plot used in FIGURE 1 become straight lines on the Compston-Jeffery plot, while points on the Compston-Jeffery plot (1959) are represented by lines in this presentation.

The fact that the four total rock measurements lie so close to a straight line is significant. It is a fundamental premise of age measurement that the system under examination has been an isolated system since the time of its formation. The four granites on which Allsopp has been working come from an area of more than 50 square miles. If there had been any process of alteration involving the addition of rubidium or strontium from outside the system, it is improbable that the amounts of rubidium or strontium added would have been in exactly the right proportions to preserve a linear relationship except in the event that the material added came from a system with the same value of the ratio  $\text{Sr}^{87}/\text{Sr}^{86}$  initially and of the same age. It is concluded from the linearity of the total rock points that the system has been closed since the time of its formation. This argument in a slightly different form was used by Schreiner in discussing total rock measurements on the Bushveld granite.

It should be noted that the ages found are those reckoned from the time the system in question became isolated. It is conceivable that at some subsequent

time the rocks have been completely remelted without addition of material from outside the system. In that case measurements on separate mineral fractions should plot along a line of smaller slope with a greater value for the initial  $\text{Sr}^{87}/\text{Sr}^{86}$ . If measurements are available for samples with different ratios of  $\text{Rb}/\text{Sr}$  in the total rock, the initial values will, of course, be different.

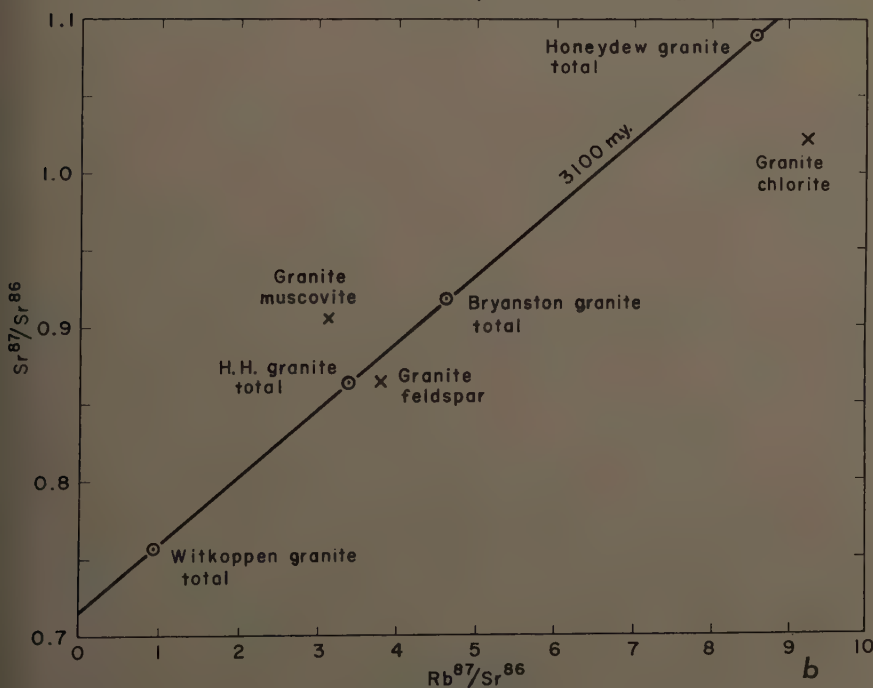
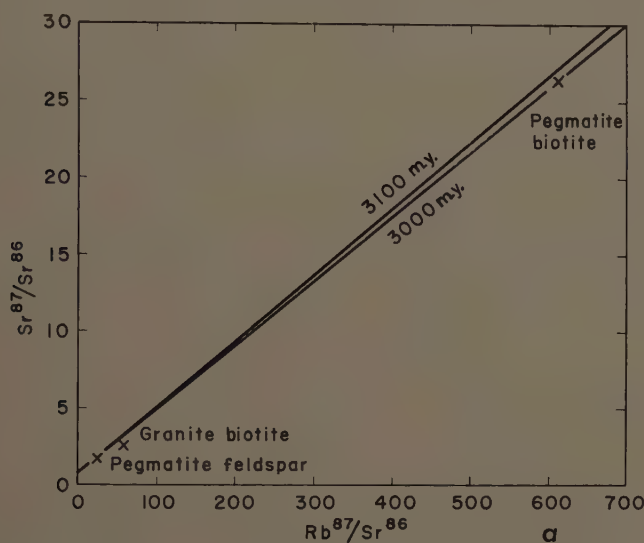


FIGURE 1.

Allsopp has made measurements on four fractions, biotite, chlorite, feldspar, and muscovite, from one of the granites. The biotite, chlorite and feldspar give consistent ages of 2300, 2400, and 2300 million years (m.y.) if the initial value of  $\text{Sr}^{87}/\text{Sr}^{86}$  is taken to be 0.740. The muscovite, however, gives an age of 3700 m.y. Assuming that the muscovite measurements are correct, the hypothesis of complete remelting at 2300 to 2400 m.y. must be discarded. The other possibility is that there has been diffusion of strontium out of the biotite and chlorite during the history of the rock. It is possible that some of this strontium has found a home in the muscovite where there is an excess of  $\text{Sr}^{87}$ . In connection with this possibility, L. O. Nicolaysen states (elsewhere in this monograph) that the biotite and muscovite are interleaved in this granite. It is therefore not unlikely that strontium diffusing from the biotite would accumulate in the muscovite. It does not seem possible now to decide between the possibilities: (1) that there has been diffusion of strontium from the biotite over the whole history of the rock, or (2) that the diffusion took place during a short period of mild metamorphism in which the muscovite was not recrystallized. It is possible that additional measurements on the calcium-rich fractions of the rock may throw some light on this point. A calculation of the amount of strontium lost by the biotite and comparison of this amount with the excess in the muscovite would be helpful, and it would be worthwhile to make measurements on the mica complex as a whole without separating it into biotite, muscovite, and chlorite.

It may be pointed out that if a biotite age is low compared with the total rock age when the same value is used for the initial  $\text{Sr}^{87}/\text{Sr}^{86}$  there must be another component in the rock for which the age so calculated is high. It may be that this component is not a particular mineral but merely the material lying adjacent to the biotite.

It was because of the possibility of diffusion of strontium from the biotite that Schreiner became interested in total rock measurement and in measurement on all possible fractions from the rock.

Allsopp has also worked on biotite and feldspar from a pegmatite occurring not far from the granite sample on which the separations were made. Using an *ab initio* value of 0.716 the ages found are 3000 m.y. G. W. Wetherill (personal communication) has also made Rb-Sr measurements on another specimen of biotite from this pegmatite and found an age of between 2900 and 3000 m.y. With the additional information from the pegmatite, there would seem to be little doubt that the age of 3100 m.y. found from the total rock measurements is the age of crystallization of the granite.

#### *Measurements on Samples of Dominion Reef Rhyolites*

These measurements from the Ottosdal area were made by Schreiner. The area from which these samples were collected was described by von Backström (1948). It was the analyses reported in his paper that led my associates and me to consider the possibility that total rock measurements could be made on these rhyolites.

The problem of the determination of the initial value of the ratio  $\text{Sr}^{87}/\text{Sr}^{86}$  arises in this case in the same way as it does in total rock measurements on granites. Schreiner used a plot of  $\text{Sr}^{87}/\Sigma \text{Sr}$  against  $\text{Rb}^{87}/\Sigma \text{Sr}$  to determine the initial value of the  $\text{Sr}^{87}$  abundance, and calculated the age from the slope of the

plot, finding an age of 3000 m.y. The age found for the rhyolites is, of course, the age since the lavas became a closed system. There are two theories of the origin of rhyolites. One of these is that the lavas were differentiated from a more basic magma not very long before the extrusion of the lavas. The other is that rhyolites represent extrusive outpourings of melted granites without admixture of other material. In the second theory, the age found by total rock measurements would be the age of formation of the granite and not the age of extrusion of the rhyolite.

In an endeavor to distinguish between these possibilities, Schreiner has made measurements on a rhyolite from the Lebombo. It is generally accepted that these rhyolites are post-Middle-Triassic in age. Schreiner's upper limit for the age is 170 m.y. Since there are no known occurrences of granites younger than 200 m.y. and older than the rhyolites anywhere in the Lebombo area, the measurements so far made favor the differentiation hypothesis, at least for this rhyolite. Measurements will be made on other samples from the area so that it will be possible to derive an initial value of the  $\text{Sr}^{87}$  abundance and a more accurate value for the age.

#### *The Total Rock Method*

In making total rock measurements it is necessary to estimate the initial value of  $\text{Sr}^{87}/\text{Sr}^{86}$  or  $\text{Sr}^{87}/\Sigma \text{Sr}$  or, alternatively, to calculate the age in such a way that the initial values do not enter into the calculation. One method of estimating the initial value of the ratios is to make measurements on some strontium-rich, rubidium-poor mineral in the rock. Another method, which we think is to be preferred, is to make measurements on total rock samples of the same granite having different ratios of rubidium to strontium. There are two unknowns: the age of the rock and the initial value for the  $\text{Sr}^{87}$  abundance, so that with two samples it is theoretically possible to calculate both unknowns. It is preferable, however, that measurements be made on more than two samples for the reason that it is then possible to apply standard statistical procedures and find not only estimates of the age and initial value of the  $\text{Sr}^{87}$  abundance but also statistical estimates of the accuracy of these quantities.

It can be shown that:

$$\frac{n_D}{n_P} = \left( \frac{\text{Sr}^{87}}{\Sigma \text{Sr}} - A \right) \left( \frac{\Sigma \text{Sr}}{\text{Rb}^{87}} \right)_w \cdot \frac{F_1}{1 - A} \quad (1)$$

where

$\left( \frac{\Sigma \text{Sr}}{\text{Rb}^{87}} \right)_w$  = ratio of strontium concentration to rubidium-87 concentration by weight;

$F_1$  = factor allowing for difference in atomic weights of Sr and  $\text{Rb}^{87}$ ;

$\frac{\text{Sr}^{87}}{\Sigma \text{Sr}}$  = ratio on number of atoms of  $\text{Sr}^{87}$  to total number of strontium atoms; and

$A$  = initial value of ratio  $\text{Sr}^{87}/\Sigma \text{Sr}$ ; or

$$\frac{n_D}{n_P} = \left( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} - B \right) \left( \frac{\text{Sr}^{86}}{\text{Rb}^{87}} \right)_w F_2 \quad (2)$$

where

$B$  = initial value of the ratio  $\text{Sr}^{87}/\text{Sr}^{86}$ ; and

$F_2$  = atomic weight factor.

For samples of the same age,  $(n_D/n_P)$  is the same constant, and may be said to equal  $C$ . It follows from 1 that

$$\frac{\text{Sr}^{87}}{\Sigma \text{Sr}} = A + C(1 - A) \left( \frac{\text{Rb}^{87}}{\Sigma \text{Sr}} \right)_w / F_1; \quad (3)$$

and from 2 that

$$\frac{\text{Sr}^{87}}{\text{Sr}^{86}} = B + C \left( \frac{\text{Rb}^{87}}{\text{Sr}^{86}} \right)_w / F_2. \quad (4)$$

Both equations represent straight lines, the slopes being  $C(1 - A)/F_1$  and  $C/F_2$  respectively.

An alternative analytical approach is to regard the equations 1 or 2 for the different samples as observational equations for the unknowns  $C(1 - A)$  and  $A$ , or  $C$  and  $B$  in the case of the equation 2, and form from them normal equations that can be solved in the usual way.

#### *Acknowledgment*

I am indebted to J. P. Buchmann of General Mining, Johannesburg, for information about the boreholes and for providing samples from the cores.

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#### *Discussion of the Paper*

G. J. WASSERBURG (*California Institute of Technology, Pasadena, Calif.*): I wonder if Hales could tell us where this locality is and what the general geology of the region is?

HALES: The samples come from the exposure of Old Granite lying immediately to the north of Johannesburg.

The Witwatersrand System dips at  $35^\circ$  roughly down to the south in the Johannesburg area and it is presumed that at some time in the past there has been updoming to the north of Johannesburg. I think that I shall pass that question on to Nicolaysen.

L. O. NICOLAYSEN (*Bernard Price Institute of Geophysical Research, Johannesburg, Union of South Africa*): In the northern part of the area, the Black Reef Series of the Transvaal System lies unconformably on the granite dome. The outcrop of this series is markedly arcuate and convex towards the north; this is a girdling effect due to the updoming of the granite. It is interesting to note that there are areas of serpentine and amphibolite at the base of the Witwatersrand System just north of Krugersdorp and that these rocks, together with other basic metamorphics, are intruded by the granite.



In 1951 MacGregor pointed out that serpentines were prominent among the oldest rocks in Southern Rhodesia. In 1955, Hess speculated that certain of these ancient serpentines represent altered remnants of the earth's primitive crust.

M. N. BASS (*Carnegie Institution of Washington, Washington, D.C.*): You mentioned that you found granite in a borehole underlying the rhyolite? Do you know what the relationship of the granite is to the rhyolite and whether it is gradation or intrusive?

HALES: It can be found out, certainly. We have looked at the complete core but it is somewhat chewed up at the boundary, and all we did was to take a sample far enough away, we thought, to be safe.

BASS: But you saw something you could interpret as a boundary within the core?

HALES: Certainly. We saw in places something we could interpret as a boundary, but we saw also other things that you could interpret as being gradational.

NICOLAYSEN: All around the sediments on the north side and the south side of the Old Granite exposure, wherever contacts are investigated, no mobilization against the granite rocks is to be seen. At all places there is an unconfusable relationship. I think that this is important, in that there are no obvious signs of remobilization of the granite during a  $\sim 2000$ -m.y.-old metamorphic event.

# AGE OF BASEMENT ROCKS IN EASTERN UNITED ARAB REPUBLIC AND NORTHERN SUDAN

Mohamed A. Gheith

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This work was done in collaboration with the Massachusetts Institute of Technology group in Cambridge, Mass., and deals with the potassium-argon dating of samples from the Eastern Desert of the United Arab Republic (Egypt).

When the available ages were plotted on a map of Africa, it was found that the northeastern third of the continent remained almost blank. The age determination of some 30 samples systematically collected from the United Arab Republic and northern Sudan, covering latitudes  $18^{\circ}$  to  $29^{\circ}$  N., was undertaken partially to fill this gap. Work has been finished on only seven of those samples, and the analyses made have been reported in the Massachusetts Institute of Technology Seventh Annual Progress Report, which has been referred to by Robert Folinsbee, University of Alberta, Canada, as the "M.I.T. telephone book." This remark has brought to mind the fact that in North Africa there are not very many "telephones," and this fact may account for the lack of ages determined from that part of the world. With increasing "phone numbers," we may hope to arrive at a better understanding of the basement rocks and a possible correlation with the rest of the continent. The difficult task of correlation of African ages is ably undertaken by L. Cahen elsewhere in this monograph.

## *The United Arab Republic (Egyptian) Basement Complex*

A look at the geological map of Africa shows that most of the United Arab Republic is covered by relatively undisturbed Cretaceous and Tertiary sediments. The only places where basement rocks outcrop are in a strip along the Red Sea coast to the east, in the southern part of the Sinai peninsula, and in Oweinat in the southwestern corner of the United Arab Republic. These basement rocks are almost always overlain by the generally nonfossiliferous Nubian sandstone series that ranges in age from upper Paleozoic to Cretaceous; they have been compared at times with the Karroo beds of South Africa.

The crystalline rocks, however, are commonly referred to, even in the most recent literature of the Geological Survey of Egypt, as "Pre-Carboniferous, most probably Pre-Cambrian" (Amin, 1954; Higazi, 1957). Hume proposed a classification of these rocks in the early part of this century that was later modified by Schürmann in several of his excellent publications on the Pre-Cambrian of Egypt. TABLE 1 is a compilation from Schürmann's (1953, 1957) and Hume's (1934) works, showing the subdivisions of these rocks.

The use of the terms Protarchean, Metarchean, and Eparchean by both Schürmann and Hume is rather unfortunate, as most of these rocks bear no resemblance to the geologists' stereotype impression of Archean rocks. It should be noted that Hume recognized only one series of granite, namely the Gattarian. Schürmann, on the other hand, later recognized a second granite

that he called the Shaitian granite, the existence of which is still doubted by some of the local geologists. Of further interest is the fact that the Hammamat series locally resembles the well-known building stone Breccia Verdi Antico. This nonfossiliferous series is believed by some geologists to be of Paleozoic age. M. M. Ibrahim of Cairo University, Cairo, United Arab Republic, for the past 10 years has been advocating a Paleozoic age for many of the granites of the Eastern Desert of Egypt.

TABLE 1  
SCHÜRMANN-HUME SUBDIVISIONS OF THE PRE-CAMBRIAN ROCKS

Gattarian	Second series granite	Calc-alkali and soda rocks; sometimes marginally gneissic.
Eparchean	Hammamat series	Sandstones and conglomerates with dioritic flows, locally contact-metamorphic; equivalent to amphibolites of Southern Region.
	—unconformity—	
	Dokhan series	Plutonic rocks similar to Gattarian. Dioritic flows, tuffs, and some sediments. Gabbro and serpentine of the Red Sea Hills and Esh-El-Mellaha Range? Probably Atalla.
	Shadli series	Schists, flows, tuffs, breccias, and sediments slightly more metamorphosed than Hammamat.
Shaitian	Old paraschists series	Metamorphic sediments, marbles; andesitic flows including red breccia. (Epizone, partly Mesozone.)
	—unconformity—	
	First series granite	Calc-alkali; rare soda rocks.
Metarchean	Atalla series	Quartzite, jasper, rhyolitic, and some andesitic flows. Baramia magnesium series (steatite, gabbro, and serpentine).
	Mitiq series	Orthogneisses, rare paragneisses, marble, mica-schists, highly metamorphic (Mesozone).
Protarchean	Fundamental gneiss (Feiran series)	Migmatites of Wadi Feiran (Katazone), ortho- and paragneisses.

### *Results and Discussion*

The accompanying map (FIGURE 1) shows the location of some of the samples collected, seven of which have been analyzed to date; the results are reported in TABLE 2. In view of these results, the stippled areas on the map perhaps should be termed Pre-Carboniferous.

The first two biotites in TABLE 2, B-3707 and B-3725, came from rocks described by geologists of the Egyptian Survey as pink granites representing the latest Gattarian intrusives. The dates determined from these two biotites differ by 78 million years (m.y.). It is noteworthy that the sample giving the younger date of 462 m.y. was gneissose, while the other showed a well-developed granitoid texture.

The third and fourth biotites came from the "gray or oligoclase granite" that is believed to be the earliest phase of the Gattarian granite. Here again the

two dates differ by 85 m.y.; the one giving the younger date of 435 m.y. is the gneissose sample while that giving 520 is the fresh-looking granitoid rock.

The above-mentioned four samples therefore represent areas being mapped as the Gattarian granite. The fifth sample is a mica schist of Metarchean age.



FIGURE 1.

However, the biotite here was badly chloritized, and we should not put too much faith in the 308-m.y. date. The last two biotite samples from the Hafafit area represent rocks that have been mapped as Protarchean, that is, as the oldest rocks of the basement complex. Again there is a difference in the dates of 54 m.y. Although the constituents of both rocks showed a preferred orientation, the one giving the younger date of 456 m.y. is definitely more gneissose.

If the difference of 11 to 17 per cent within each pair and the fact that the gneissose samples gave the younger dates in all three cases are taken to be significant at all, then several explanations come to mind. The possibility of a younger intrusive not yet encountered cannot be excluded. Surface and near-surface agencies can account for age differences of this magnitude as J. Lawrence Kulp mentions elsewhere in this monograph. Another possibility, based on G. W. Wetherill's discussion, also in this publication, would be the inheritance of radiogenic argon.

From all the results shown in TABLE 2, the dates given, ranging from 435 to 540 m.y., are quite reminiscent of the dates determined from the Mozambiquian Belt that extends north to south in the eastern part of southern Africa almost in a straight line with the samples of this investigation. Analyzing samples

TABLE 2  
ARGON AGES ON BIOTITES FROM THE EASTERN DESERT, UNITED ARAB REPUBLIC

Samples	Location	K (%)	Ar <sup>40</sup> /K <sup>40</sup>	Air correction (%)	Age (m.y.)
B-3707	Just west of Gebel Nugrus	3.93	0.0306	20	462
B-3725	Wadi Essel	5.00	0.0372	5.7	540
B-3711	7 km. south of Gebel Mueilha	5.67	0.0360	12	520
B-3723	Wadi Abu Had	5.50	0.0286	12.6	435
B-3714	1½ km. south of Gebel El Maiyit	1.56	0.0196	40	(308)*
B-3716	Hafaft Mine area	4.85	0.0352	8.3	510
B-3719	Hafaft	6.92	0.0302	6.3	456

\* Badly chloritized.

from Sudan will clarify the possible relation between the Mozambiquian Belt to the south and the Red Sea mountains to the north.

Using the extended Paleozoic time scale, the dates presented here would fall in the upper Cambrian or lower Ordovician. This is rather significant in view of the absence of lower Paleozoic sediments from northeastern Africa (unless the Hammamat series is of that age, as previously mentioned).

I have recently received a copy of a paper by Higazy and El-Ramly (1960) that reveals that isotope analyses (mostly on total rock) were made by S. B. Brandt and G. D. Afanasiev at the Dagestan section of the Academy of Sciences of the Union of Soviet Socialist Republics, Moscow, U.S.S.R. The dates obtained, ranging from 600 to 40 m.y., are taken to represent actual ages of igneous intrusions and volcanic activity, ranging from Eo-Cambrian to Tertiary respectively. Two samples similar to samples B-3707 and B-3723 (TABLE 2), which gave dates of 462 and 435 m.y., gave Higazy and El-Ramly the strikingly similar dates of 460 and 450 respectively (as was noted by the latter authors).



*Acknowledgments*

I am grateful for the invaluable assistance and interest of R. Higazi, Undersecretary of Industry, United Arab Republic, in collecting and sending the samples. I am grateful also to El-Shazly, El-Ramly (1955), and their colleagues in the Geological Survey of Egypt, and M. I. Faris and M. M. Mourad of Ain Shams University, Cairo.

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# REVIEW OF GEOCHRONOLOGICAL KNOWLEDGE IN MIDDLE AND NORTHERN AFRICA

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## Introduction

This paper summarizes the present state of geochronological knowledge in that part of Africa situated north of South West Africa, Bechuanaland Protectorate, Southern Rhodesia, Nyassaland, and Mozambique.

The geochronology of this very large area is still in an exploratory phase and, except for a single orogenic belt of great mineral wealth, no sufficiently systematic work describing it has been published.

Nevertheless, roughly 400 isotope analyses on African minerals are available, of which nearly one half are for the area covered in this summary. Of the total number more than one third are common lead isotope analyses.

This far from negligible amount of work has been carried out with the help of several laboratories located in North America that have willingly joined forces with the few European and African laboratories devoted to this work.

For the territories of middle and northern Africa, it has been necessary to create the tools before carrying out systematic research. This has been going on for some time and, particularly in Great Britain and Belgium, systematic research has begun or is about to begin.

This paper therefore may be regarded as summarizing a picture obtained by nonsystematic work that in many cases was carried out in the early stages of each technique. The above-mentioned prospects give reason to hope that within a few years this picture will be greatly improved.

Geochronological results in the vast area under review are very unevenly distributed: they are mainly focused in an area composed of east Africa, Northern Rhodesia, and the eastern part of the Republic of the Congo.\* A second area giving a certain number of results runs along the west coast from the river Congo to south Cameroons. Only a few results of geochronological value are scattered through the remaining portion of the continent.

The following areas will be examined successively (FIGURE 1): Katanga and Northern Rhodesia; the region surrounding Lake Tanganyika; east Africa (Tanganyika, Kenya, and Uganda); north Congo; the west coastal area from the river Congo to the southern Cameroons; west Africa; the northern part of Africa.

For each of these areas a summary of the rock succession and valid geochronological data are given and summarily discussed. Anomalous common lead isotope analyses and some isolated results of unknown or uncertain geological significance are omitted. The terminology is that currently in use in the territories concerned. Geological references are, in principle, limited to one or two

\* The Republic of the Congo is the former Belgian Congo; the Congo Republic is part of former French Equatorial Africa. In expressions such as "east Congo," Congo designates the former Belgian Congo.

recent publications for each area. References to geochronological results are complete.\*

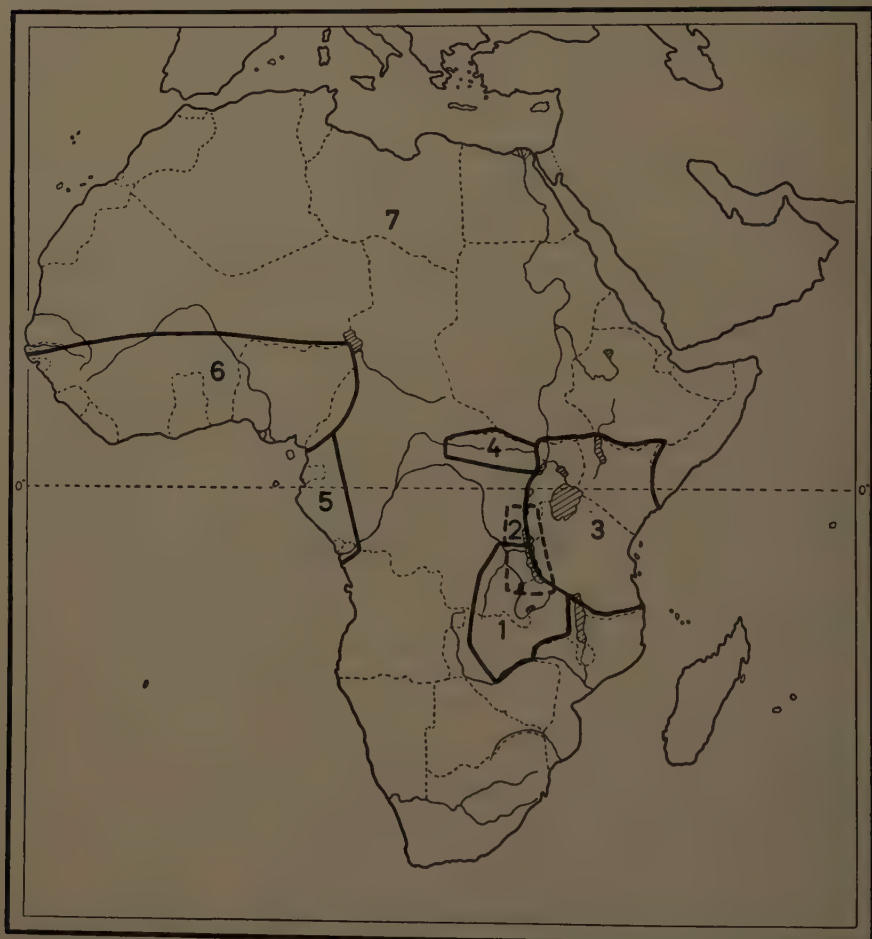


FIGURE 1. Areas with geochronological data: (1) Katanga and Northern Rhodesia; (2) the region surrounding Lake Tanganyika; (3) east Africa; (4) north Congo; (5) the west coastal area from the river Congo to the southern Cameroons; (6) west Africa; (7) the northern part of Africa.

### Review of Geochronological Knowledge in Middle and Northern Africa

#### KATANGA AND NORTHERN RHODESIA

This area is world-renowned for its rich mineral wealth in copper and other minerals, including uranium.

\* Data complete to July 1956 were published earlier (Holmes and Cahen, 1957). The lead isotope ages are read from the tables recently published by Stieff *et al.* (1959). Constants used in the other methods are given in the paper by Holmes and Cahen.

## Geology

The copper belt is a fold belt of arcuate shape with a southeastern trend to the east and a west-southwestern one to the west. Toward the outer rim of the arc, the folded beds pass gradually to the flat-lying formations of the foreland.

The rocks involved in this belt are collectively known as the Groupe du Katanga.

TABLE 1  
KATANGA (AND NORTHERN RHODESIA) SUCCESSION\*

Upper Carboniferous and Permian, *Série de la Lukuga*: Tillite (equivalent to Dwyka Tillite) at base  
Major unconformity

(15) Uranium phase 3(?): southeast Katanga, Northern Rhodesia, 520 m.y.  
(14) Slight folding, faulting and similar actions  
(13) Uranium phase 2b: Kalongwe, Luishya, † 615 m.y.  
(12) Uranium phase 2a: Shinkolobwe (?), Swambo, † 625 m.y.  
(11) Post Upper Kundelungu thrust faults probably continuing, perhaps intermittently, to 14 (fault planes are slightly folded)  
(10) Uranium phase 1 Musonoi., undated†  
(9) Folding

Groupe du }  
Katanga }  
Système du }  
Kundelungu } (8) Série du Kundelungu supérieur§ et du Kundelungu moyen  
(7) Petit conglomérat ('Tillite')  
(6) Unconformity  
(5) Série du Kundelungu inférieur

(4) Disconformity  
(3) Système du Grand Con- { Série de la Tillite du Grand Conglomérat  
glomerat et de Mwashya { Série de Mwashya  
(2) Slight unconformity  
(1) Système de Roan { Série supérieure, including "Série des Mines"  
{ Série inférieure

Muva System. Northern Rhodesia and southeast Katanga  
Kibara System. Central and northern Katanga

\* This table gives the succession as tabulated in Katanga. There is no general agreement as to the subdivision of this succession. This table follows Cahen (1954). The upper portion of the succession (Kundelungu System) is given in more detail than the lower.

† These two phases may not be distinct.

‡ The position given here is relative to uranium phase (No. 1 is tentative).

§ The uppermost Kundelungu is known only in regions where no real folding (9 and 11) has occurred; the slight undulations that have been measured are parallel to the main folds. Although it might be possibly later than 10 and 11, it is likely that it is older than 14.

In central and northern Katanga, the flat-lying beds of the Katanga System lie unconformably upon an important fold belt of northeastern trend, the Groupe des Kibara, which toward the northeast changes its name to Groupe de l'Urundi, which is the east Congo name for the Karagwe-Ankolean System of Uganda.

In southeast Katanga and the northern part of Northern Rhodesia, the folded beds of the Groupe du Katanga rest unconformably on that part of the upper basement of Northern Rhodesia called the Muva System.

The succession of events is retraced in TABLE 1.

*Geochronology*

*Katanga System.* The orogeny that deformed the beds involved in the copper belt was accompanied and followed by uranium occurrences, including the development of the well-known mine of Shinkolobwe. The age of these ores has been and is being systematically studied. Conventional ages of a certain number of lead occurrences are also known.

Three groups of ages appear to be present. The age of certain uranium occurrences, the most important being Shinkolobwe, is  $625 \pm 20$  million years (m.y.). The value chosen is that given by concordant results that agree well with the "best" ages obtained on numerous, slightly discordant samples. The age of the slightly discordant Kalongwe and Luishya uraninites is  $615 \pm 20$  m.y. (Ledent, 1956 and 1958). These values may in reality belong to the same group as the Shinkolobwe age, but Derriks and Oosterbosch (1958) have reason to believe them to be distinct.

The concordant age of uraninites and brannerite of Nkana, Kansanshi and probably other occurrences in southeast Katanga and Northern Rhodesia is  $520 \pm 20$  m.y. (Darnley, 1960; Horne, 1960; Ledent, 1958).

Model ages of lead from galenas emplaced in sediments of the Groupe du Katanga range from 430 to 590 m.y. in Katanga and from 400 to 687 m.y. in Northern Rhodesia\* (Wilson *et al.*, 1954; Eberhardt *et al.*, 1955; Holmes and Cahen, 1957).

The position of the Katanga uranium mineralization in the stratigraphical column has long been in dispute. Derriks and Vaes (1955) have shown that the Shinkolobwe uraninite was introduced after the major thrusts. These thrusts occurred at a late stage in the orogeny after most and perhaps all the Upper Kundelungu had been deposited. Some movements occurred after the Shinkolobwe, Kalongwe, Luishya, and other mineralizations, whereas the dated Nkana and Kansanshi and other mineralizations of 520 m.y. seem to be entirely posttectonic.

The same thing is probably true of most of the lead occurrences that are chiefly found in posttectonic veins and that, if Broken Hill (687 m.y.) is omitted, all range from 400 to 590 or  $500 \pm 100$  m.y. (the average value is 507 m.y.).

*Groupe des Kibara.* Ages of micas from two pegmatites (Manono and Muika) by K-Ar and Rb-Sr (Aldrich *et al.*, 1958) and reasonably concordant ages on priorite from a vein linked with a granite batholite from a third locality Mitwaba (Ledent *et al.*, 1956; Eberhardt *et al.*, 1956) are all compatible with an age of  $1000 \pm 50$  m.y.

Two common lead model ages from galena occurring in veins, some of which also contain the priorite, are in keeping with these results:  $850 \pm 40$  (Eberhardt *et al.*, 1956) and  $925 \pm 70$  m.y. (Geiss, 1954).

Ages of granites of the Kibara belt are now being investigated.

The granite batholites are considered to be late orogenic; the pegmatites are

\* All common lead ages are here computed following the Holmes-Houtermans model. Some published common lead-isotope analyses from the Geophysical Laboratory, Toronto University, Toronto, Canada (Holmes and Cahen, 1957), have since been slightly modified. In these cases, the model ages quoted here are derived from the modified analyses and may be slightly different from those previously published.



considered either to belong to the same phase of activity or to be somewhat younger.

The results thus far obtained are therefore linked with a late phase in the orogeny.

In northeast Katanga and Kivu the Groupe des Kibara rests unconformably on the Groupe de la Ruzizi, which is provisionally dated at ca. 1600 m.y. or older.

*Muva System and basement of Northern Rhodesia (Irumi belt).* The only age determinations in these rocks are on monazite, respectively alluvial and concentrated from quartzites of the Muva System (O'Brien, 1958). Both results are too discordant for secure interpretation.

*Summary.* This central African area shows the succession of two well-dated belts. A late phase of the orogeny that crowned the younger Katangan belt occurred at about 625 m.y. Some posttectonic events took place at about 520 m.y.

This younger belt rests unconformably on the Kibaran belt; a late phase of this Kibaran activity is dated at  $1000 \pm 50$  m.y.

The Kibaran belt itself is known to be younger than the Ruzizi-Ubendian belt of ca. 1600 or older (see under *Groupe des Kibara*, above).

#### THE REGION SURROUNDING LAKE TANGANYIKA

The area concerned comprises the eastern portion of the former Belgian Congo, Ruanda-Urundi, a portion of Northern Rhodesia, the western margin of Tanganyika, and Uganda. Its axis is formed by Lakes Tanganyika and Kivu in the western Rift Valley.

#### Geology

Two important geosynclinal belts, the Ubendian-Ruzizi and the Kibara-Urundi-Karagwe-Ankolean, cross each other and are wedged in between older masses, the Dodoman and Nyanzian "shield" to the east, the pre-Kibaran rocks of the Kasai-Lomami "shield" to the southwest, and the ancient north Congo "shield" to the northwest.

We are here concerned with the two orogenic belts. The older of these is the Ubendian of Tanganyika Territory, that may be followed into the Republic of the Congo and Ruanda-Urundi under the name of the Groupe de la Ruzizi (Cahen, 1952; Quennell, 1956).

Pelitic and psammitic metamorphic rocks predominate; there is a great development of biotite gneiss, and limestone is also present. Migmatitization is widespread. Over most of its extension this belt has a southeast to northwest trend.

The rocks forming the younger belt with a predominantly southwest to northeast trend are known in Katanga as the Groupe des Kibara; in east Congo and Ruanda-Urundi they have been called Groupe de l'Urundi and in Uganda, the Karagwe-Ankolean System.

To the southwest of Lake Kivu the unconformable superposition of the Groupe de l'Urundi on the Groupe de la Ruzizi is now well known (Lhoest, 1946; Safiannikoff, 1950). In some other areas the contacts between the two belts are rift faults, the older belt lying in the uplifted areas (Cahen, 1952).

North of parallel 2° south, both belts adopt a southeast to northwest trend, and their delineation is far from having been clarified.

To the west the Kibara portion of the younger belt rests upon older rocks of the Kasai shield, whereas the Karagwe-Ankolean is unconformably superimposed on older formations, which McConnell equates with his Buganda Group cited in the discussion of east Africa (see below).

The Kibara-Urundi-Karagwe-Ankolean belt consists mainly of schists of light-grade metamorphism and relatively pure quartzites. Some arkosic rocks and limestones are also present. Contact metamorphism zones surround the abundant late-orogenic granites that, with pegmatites, occur throughout the belt.

Gold is the principal mineralization linked with the older belt, whereas the Kibara-Urundi-Karagwe-Ankole belt is the host of an important tin, niobium-tantalum and tungsten mineralization.

### *Geochronology*

*Kibara-Urundi-Karagwe-Ankole belt.* It has already been observed that the southeast Kibara portion of this belt contains a certain number of well-dated minerals that indicate an age of  $1000 \pm 50$  m.y. for a late phase of the orogeny.

In the Urundi portion of the belt (eastern Congo and Ruanda-Urundi), numerous minerals are being dated. The only results at hand are the model ages of two galena leads located in Maniema,  $960 \pm 50$  m.y. (Eberhardt *et al.*, 1956), and Kivu, 850 m.y. (Wilson *et al.*, 1954), respectively. The isotopic composition and model ages of these leads are completely in keeping with those of the Kibaran galena leads mentioned earlier that are found in veins, some of which also contain the well-dated Mitwaba priorite of  $1045 \pm 50$  m.y.

These data, although insufficient, do confirm the obvious geological continuity between the Kibara and Urundi portions of the belt. The same may be said of the Karagwe-Ankolean of the type area in Uganda that is in continuity with the Urundi of Ruanda-Urundi. The only age determination is a Rb-Sr measurement on a lepidolite from a pegmatite from near Ruhuma (Kigezi) that gives an apparent age of  $800 \pm 10$  per cent m.y. (Davis *et al.*, 1958). This result, however, is considered rather unreliable owing to the poor quality of the material.

Other results in the same general area are obtained on minerals that either occur in rocks that do not certainly belong to this belt, or give unreliable results, or visibly belong to a younger cycle.

*Ubendian-Ruzizi belt.* In this belt also, age determinations are few and far between. They fall into two groups: an older group of ca. 1600 m.y. and a younger group of ca. 1000 m.y. (the range involved in "ca." is approximately 100 m.y., but it is better not to express it in figures as some results are still provisional).

The older group consists of a galena lead (1550 m.y.) located in the vicinity of MPanda, Tanganyika Territory (J. W. L. de Villiers, unpublished analysis), and another (1580 m.y.) located in the vicinity of Usumbura, Urundi, more than 300 km. to the northwest (R. M. Farquhar, unpublished analysis). The lead mineralization near MPanda may be associated with posttectonic potash granite. An incomplete and unpublished age determination (Sr-Rb) on feld-

spar from the latter indicates that it falls into this older group (G. D. L. Schreiner).

Pending further investigation, about 1600 m.y. can be taken as the age of a late phase of activity of the Ubendian-Ruzizi belt. The Ubendian orogeny may be older.

The younger ages (about 1000) obtained by Ar-K and Rb-Sr on muscovite from a pegmatite near Karema, Tanganyika, (Aldrich *et al.*, 1958) and on a galena lead from veinlets to the north of Albertville, north Katanga, Republic of the Congo, show that these rocks and mineralizations may be considered as manifestations of Kibara-Urundi-Karagwe-Ankolean activity ( $1000 \pm 50$ , see above), and they are much younger than the Ubendian-Ruzizi activity proper.

An apparent age of  $2100 \pm 250$  m.y. ( $\text{Pb}^{207}/\text{Pb}^{206}$ ) apparent age on a detrital monazite near Astrida, Ruanda (Holmes and Cahen, 1957) needs support before conclusions can be drawn.

*Summary.* Two belts are considered in this paragraph. A postorogenic phase of the older, Ubendian-Ruzizi belt is dated about 1600, and a late orogenic phase of the younger belt is dated about 1000. Only the southeast (Kibara) portion of this Kibara-Urundi-Karagwe-Ankolean belt is more or less adequately dated. More work is needed (and is being carried out) on the central and northeastern portions of the same belt and in the Ubendian-Ruzizi.

#### EAST AFRICA (TANGANYIKA, KENYA, AND UGANDA)

Although portions of this area are also reviewed in paragraphs above and below, this section attempts to give a general commentary on geochronological data in these three territories.

#### Geology

Pre-Cambrian stratigraphy of these three territories is summarized in TABLE 2, where the successions given are those officially adopted by the three geological surveys.

In TABLE 2 (and in the following tables) single lines represent correlation, double lines physical continuity.

Differences of opinion between the three surveys are immediately apparent.

*Usagaran of Tanganyika and basement system of Kenya.* These two terms respectively cover the Tanganyika Section and the Kenya Section of the "Mo-zambique belt" of Holmes (1951). They are thus in physical continuity. However in one territory they are considered older than the Kavirondian and Nyanzian; in the other they are considered younger. The former is the traditional view; the latter was introduced in 1948 by Holmes (1951).

*Nyanzian and Kavirondian of Tanganyika and Kenya, Samia series, Bulugwe series, and Buganda series of Uganda.* Whereas in Tanganyika and Kenya, the Nyanzian and Kavirondian are considered definitely older than the Karagwe-Ankolean, the Uganda Geological Survey believed, chiefly on lithological grounds, that the Buganda metasediments (or series) are to be correlated with the Karagwe-Ankolean (Pallister, 1956).

On the basis of the almost physical continuity and general similarity of the

TABLE 2  
SUCCESSIONS IN EAST AFRICA

Western Uganda (Pallister, 1956)	Tanganyika (Quennell <i>et al.</i> , 1956)	Kenya (Pulfrey, 1956; McCall, 1958)	Eastern Uganda (Pallister, 1956)	Central Uganda (Pallister, 1959)
Singo series (?) and Bunyoro series	Basic igneous activity Bukoban	(?) Basic igneous activity Kisii series		Singo series
Granites, pegmatites, and metamorphism; Karagwe Ankolean	Granites, pegmatites, and metamorphism; Karagwe Ankolean		Granites; (Samia series (Bulugwe series)	Pegmatites; Buganda series
Igara schists (part of former Toro system)	Migmatization and metamorphism Ubendian and Usagaran Granites Kavirondian	Granites Kavirondian		
"Basement complex" (including Toro quartzite) and west Nile group.	(?) Granites Nyanzian Migmatization and metamorphism Dodoman	Granites Nyanzian Migmatization and metamorphism basement system		Basement complex (undifferentiated)

Samia and Bulugwe series with the Buganda series, this correlation is extended to the Samia and Bulugwe series that are continuous with the Kavirondian-Nyanzian of Kenya (Pallister, 1956). A recent discussion of this question may be found in Cahen (1952), McConnell (1959), and Pallister (1959).

*The Ubendian and Usagaran.* These are considered in Tanganyika two portions of the same belt. This correlation was officially put forward in 1956 (Quennell). It had also been considered by Cahen (1952).

### *Geochronology*

A certain amount of geochronological work has been carried out on these formations of east Africa. Although insufficient to solve all above-mentioned problems, the work done has thrown light on the situation.

*Ages in the Usagaran of Tanganyika and basement system of Kenya.* All ages obtained thus far are young. They fall under two groups.

(1) Pegmatite minerals and porphyroblasts in migmatites in the basement system of Kenya: one concordant result on samarskite from Tura (Holmes and Cahen, 1955) is  $465 \pm 20$  m.y.; five Ar-K determinations on feldspar from pegmatites and migmatites (410 to 490 m.y.) average 452 m.y. (two of these observations are unpublished and communicated by E. P. Saggerson, the others, obtained by H. A. Shillibeer and K. Watson, were reported by Holmes and Cahen, 1955 and 1957).

(2) Uraninite from Morogoro, Uluguru, Tanganyika and samarskites from Turkana province, Kenya: uraninite is found in pegmatites in the Usagaran of Tanganyika. Concordant determinations lead to an age of  $615 \pm 20$  m.y. (Holmes and Cahen, 1955). The samarskites come from pegmatites in the "basement" of Kenya and have an age (based on a concordant determination) of  $636 \pm 20$  m.y. (Darnley, article in press).

In Mozambique and Nyassaland the same belt contains pegmatites from which minerals have been dated in the same age range.

Taken as a whole, the above information shows the youngest metamorphism of this belt to be ca. 465 m.y. (migmatitization and pegmatites); earlier pegmatites are the same age as the Katanga uraninites.

More work is necessary before it can be decided that this is the age of the belt as a whole. The situation may be that of the Mayumbe belt of the west coast, in which a younger activity of about 475 m.y., including migmatitization and pegmatites, is superimposed on a much older belt (as discussed below).

*Ages in the Karagwe-Ankolean belt.* As already mentioned, the only age in indubitable Karagwe-Ankolean rocks of Uganda is an Rb-Sr determination on rather poor material (mica). The age obtained is  $800 \pm 10$  per cent m.y. Other portions of the same belt give more reliable ages in the range  $1000 \pm 50$  m.y.

*Ages in the Ubendian-Ruzizi belt.* As mentioned earlier, the age of a post-tectonic phase of activity in the Ubendian-Ruzizi belt can provisionally be expressed as ca. 1600 m.y. The Ubendian orogeny may be older. Activity of Kibara-Urundi-Karagwe-Ankolean ages is also present in this belt.

*Ages in the Buganda series of Uganda and in the Kavirondian and Nyanzian Systems.* Muscovite from pegmatites at Lunya and Nampeyo yield Rb-Sr



ages of  $1870 \pm 10$  per cent and  $1840 \pm 10$  per cent m.y., respectively (Davis *et al.*, 1956).

Muscovite from a third pegmatite at Mbale, in an area that links the Buganda series to schists formerly included in the Toro System, yields by the same method  $1870 \pm 10$  per cent m.y. (Davis *et al.*, 1956).

There are no true ages in the Nyanzian and Kavirondian Systems. However three model ages 2790 to 2825 m.y. have been obtained on lead from galenas in gold reefs of the Kenya-Uganda border.

The reefs are post-Nyanzian, but one reef is certainly pre-Kavirondian; another cuts the Masaba granite that is considered intrusive in both the Nyanzian and Kavirondian.

*Ages in the Dodoman System.* Several Rb-Sr determinations on lepidolite from Hombolo pegmatite, which occurs in one of the type areas of the Dodoman, give ages ranging from 2250 to 2440 m.y. (Davis *et al.*, 1956; Jamieson and Schreiner, 1957).

### Discussion and Summary

Fragmentary as it is, the evidence supplied by existing age determinations does lead to conclusions that throw light on the contradictory sequences shown in TABLE 2.

There is no geochronological evidence that favors correlation of the Ubenidian and Usagaran of Tanganyika (or basement of Kenya). However, both appear to be younger or, at least, the dated phases of activity in these two belts are younger than the Kavirondian, Nyanzian, and Dodoman.

The correlation favored by the Geological Survey of Uganda between the Buganda series and the Karagwe-Ankolean is plainly in error. There is no reason to doubt the evidence supplied by the three concordant Rb-Sr determinations on micas from pegmatites in the Buganda series.\*

Although the correlation of the Buganda series with all or part of the Bulugwe series and Samia series of east Uganda (Nyanzian and Kavirondian of Kenya) is unanimously accepted (the two patches of metasediments are almost continuous and very similar in all respects), some discussion may arise over the precise correlation: Is the Buganda series equivalent to the Bulugwe or Nyanzian alone (Pallister, 1959), or with both the Bulugwe and Samia series, or Nyanzian and Kavirondian (McConnell, 1959)? The map and lithology of the rocks involved seem to indicate that this second hypothesis is more likely.

The Kavirondian System, despite its unconformable relationship with the Nyanzian System, is generally regarded as a kind of Molasse of the latter, and "it is believed that the Kavirondian rocks are in fact not very different in age from the Nyanzian rocks" (Quennell, 1956).

\* J. W. Pallister, although recording the ages of two of these micas, writes: "The method is liable to considerable error and these ages cannot be too closely relied upon unless corroborated by other radioactive methods." This opinion was perhaps founded on what Holmes and Cahen had written (1955). At that time such an opinion was based upon results that included those exploratory results determined by Ahrens' spectroscopic technique; there was also a conflict between scales obtained by U-Pb and Rb-Sr caused by the erroneous value of the decay constant of Rb<sup>87</sup>. At present the status of the Rb-Sr method is greatly improved and, although more work is needed to date these belts, there is no reason to cast doubt upon these three ages.

It seems however that the main reason for this opinion is the field relation between the two systems. The Kavirondian is always associated with the Nyanzian. However in most of Tanganyika the Nyanzian is seen alone.

There seems to be room for the possibility that these two systems are quite distinct\* and that the appearance of unity may be no more than the result of the action of the second orogeny on the two systems.

In this case it is tempting to assume that whereas the pegmatite micas of 1840 to 1870 m.y. characterize the younger orogeny, the galena-lead model ages may "date" the older one at ca. 2800 m.y. It may be significant that one of these reefs is post-Bulugwe (Nyanzian) and pre-Samia (Kavirondian).†

It is worth recalling that great analogies exist between the Nyanzian of Tanganyika and Kenya and the Bulawayan of Southern Rhodesia (Macgregor, 1951). It is therefore interesting to find that the three above-mentioned galena leads have precisely the same isotopic composition as a host of other galena leads located in the Bulawayan (Holmes and Cahen, 1957).

TABLE 3

Age (m.y.)	Evidence
465-636	Basic igneous activity; Bukoban (not dated, correlation)* Migmatitization and metamorphism; Usagaran (in part?; this belt may be multicyclic)†
1000	Granites and pegmatites; Karagwe-Ankolean
1600	Potash granite and veins; local migmatitization and metamorphism; Uben-dian
1870	Batholiths and pegmatites; Buganda (and Kavirondian)
2250-2440	Pegmatites, migmatitization, and other forms; the Nyanzian probably and the Dodoman certainly are older than this approximate age limit

\* Western east Africa.

† Eastern east Africa.

In Southern Rhodesia the model ages of the galena leads are supported by reliable age determinations by other methods.

At present, although the Hombolo pegmatite in the Dodoman is certainly older than the three pegmatites in the Buganda series there is as yet no corroboration of the presumption that the Dodoman is older than the Nyanzian. Geologists in Tanganyika are "coming to believe that the Nyanzian may in fact be a member of the Dodoman" (Quennell, unpublished observation).

A summary of present geochronological evidence favors the sequence in east Africa shown in TABLE 3.

#### NORTH CONGO

The area under examination is limited in the west by the meridian 22° east Greenwich, in the east by the Nile, in the north by the northern frontier of the

\* This is supported by recent work in south Nyanza, Kenya (McCall, 1958) that shows an angular unconformity between Kavirondian and Nyanzian. There are post-Nyanzian and pre-Kavirondian granites and post-Kavirondian granites. McCall distinguishes both a post-Nyanzian and a post-Kavirondian orogeny.

† If this hypothesis is correct, one of these leads would have migrated to its reputed post-Samia position or the Masaba granite would be composite (part post-Bulugwe and pre-Samia, part post-Samia).

Republic of Congo, and, to the south, by the northern limit of the Mesozoic sediments of the Congo basin.

In this vast area geological knowledge and geochronological data are scarce. However, such geochronological information as does exist to date is of interest and is in keeping with current geological views.

### *Geology*

The accepted sequence (Cahen, 1954) is: (1) Formation du Nil Occidental (west Nile group of Holmes, 1951) and its probable equivalent, Formation du Bomu; (2) Formation de la Gangu; (3) Groupe du Kibali, and (4) Groupe de la Lindi.

### *Geochronology*

A small number of galena-lead model ages are recorded.

One, located in a vein cutting through an unfaulted remnant of the Groupe de la Lindi at Mount Homa, gives a model age of 660 m.y. (Wilson *et al.*, 1954).

Two others, in gold reefs located in the Groupe du Kibali near Watsa, yield an average model age of  $1840 \pm 100$  m.y. (Wilson *et al.*, 1954; Eberhardt *et al.*, 1956).

The last two, located at Kokosho near Kule Matundu in gold reefs of the Formation de la Gangu, yield model ages of  $3340 \pm 50$  and  $3430 \pm 60$  m.y., respectively (Wilson *et al.*, 1954; Eberhardt *et al.*, 1955). These last leads have almost identical isotopic compositions to that of the well-known lead from Rosetta Mine in South Africa. These are the oldest leads yet discovered in geological formations.

### **Discussion and Summary**

The Groupe de la Lindi has always been correlated with the Groupe du Katanga and other similar formations. It may therefore be said that the presence of a lead of Katanga age is in keeping with this correlation.

The two galena leads from near Watsa have conventional ages,  $1840 \pm 100$  m.y., which recall the Rb/Sr ages from pegmatites of the Buganda series of Uganda as discussed above ( $1840 \pm 10$  per cent,  $1870 \pm 10$  per cent m.y.); this corroborates the views put forward by Holmes (1951), Cahen (1952), and recently advocated by McConnell (1959) of a correlation between Kibali-Toro System\* and Buganda schists-Kavirondian System and Nyanzian System.

The more localized correlation between Kibali and Toro had earlier been put forward by Combe (1944).

The geochronological data seems to imply that the youngest orogenic activity implicating the above-mentioned systems occurred at about 1850 m.y. However some of the formations involved may be much older (as discussed above).

The third group of conventional ages corroborates Holmes' opinion (1951) that the west Nile belt is an extremely old belt.

\* The schists formerly allocated to the Toro System are now shown to be most probably equivalent to the Buganda series or group. The Toro quartzite that, together with the schists forming the Toro System, are probably older. The name Toro System is therefore in the process of being abandoned (McConnell, 1959).

THE WEST COASTAL AREA FROM THE RIVER CONGO  
TO THE SOUTHERN CAMEROONS

This area comprises, from south to north, the western portions of the following territories: the Republic of Congo (Bas-Congo), two portions of what was known as French Equatorial Africa (the Congo Republic and Gabon), and the southern Cameroons.

*Geology*

The geology of this area, especially in the south, is relatively well known. However correlations between the northern and southern portions are a little uncertain (Cahen, 1954; Gazel *et al.*, 1956; Gérard, 1958).

The succession of events in the southern portion (the Republic of Congo and the Congo Republic) is summarized in columns 1 and 2 of TABLE 4, that of events in the north is to be found in columns 3 and 4 of the same table.

*Geochronology*

A certain number (more than 30) of age determinations are available. However, with the exception of five agreeing Ar-K determinations, the other results are individual lead-alpha apparent ages and common lead model ages. In view of the unreliability of the latter two methods, only those results supporting each other are used. Isolated results by these same methods are not considered trustworthy enough to be mentioned.

Results fall into five main groups: (1) about 2500 m.y., (2) about 1200 to 1500 m.y., (3) about 660 m.y., (4) about 475 m.y., and (5) about 350 m.y.

*The 2500-m.y. age group.* This is represented by two lead-alpha apparent ages on zircon from granites belonging to or cutting through the "basement complex" of the southern Cameroons, 2500 m.y., and northern Gabon, 2490 m.y. (Roques, 1956), and one common lead conventional age of  $2460 \pm 70$  m.y. in similar rocks a little to the south (P. Eberhardt, personal communication).

*The 1200 to 1500-m.y. age group.* This group comprises four lead-alpha results spreading from 1180 m.y. to 1480 m.y. Three of these results are from zircons in granites or diorites of the Mayumbe belt in the Republic of Congo (M. Roques, unpublished observations) and the Congo Republic (Bessoles *et al.*, 1956). If the spread of results is taken as indicating the possibility of some loss of lead, the age of the Mayumbe belt might be older than 1480 m.y. Two lead-alpha apparent ages of the same order of magnitude, 1292 and 1466 m.y. (Roques, 1956) are also known from Gabon in granitic rocks, the latter at least in formations considered equivalent to the Mayumbe belt. In this general area two further results that may possibly be included in this age group are known: a lead-alpha apparent age on alluvial zircon, 1785 m.y. (Roques, 1956) and a common lead conventional age,  $1710 \pm 50$  m.y. (P. Eberhardt, personal communication). The latter comes from a vein or lense in the "Mitendi series" that is also generally considered as more or less equivalent to the Mayumbe belt.

The conclusion that may be drawn from this not very trustworthy evidence is that the Mayumbe belt granites are probably older than 1480 m.y. and that



TABLE 4

Lower Congo (Cahen, 1954; Bertossa and Thonnart, 1957)	Republic of Congo, (Gérard, 1958)	Gabon, Ogooué (Gérard, 1958)	South Cameroons (Gazel <i>et al.</i> , 1956)
Pb mineralization: $\pm 350$ m.y. Noqui riebeckite-aegyrine granite Postschisto-gréseux orogeny: Thrusts Folding m.y. $\pm 475$ m.y. Faults + Cu-Pb-Zn mineralization $\pm 660$ m.y. Schisto-gréseux system: Série de l'Inkisi, disconformity Séries de la Mpioka et de la Mfidi, disconformity Schisto-calcaire system: Slight disconformity Tillite supérieure du Bas-Congo: Disconformity Haut-Shilango-Loula system: Disconformity Tillite inférieure du Bas-Congo (with lavas): Slight unconformity Sansikwa system*	Pb mineralization: $\pm 350$ m.y. Postschisto-gréseux orogeny: Folding Faults + Cu-Pb-Zn miner, $\pm 660$ m.y. Série de l'Inkisi Disconformity Série de la Mpioka Disconformity Série schisto-calcaire Slight disconformity Tillite supérieure du Bas-Congo: Slight disconformity Séries de la Loula et de la Bouenza: Tillite inférieure du Bas-Congo (with lavas): Slight unconformity Série de la Mossouva*	Série gréseuse de la Noya Disconformity Série calcaire de la Noya Disconformity Complexe tillitique de l'Aming	Complexe tillitique de Dia et de la Bandja (with lavas) Séries de Nola, du Beuk et de Sembe- Ouesso*

Groupe du Congo occidental



Post-Mayumbe orogeny and granites: Pb/ $\alpha$ results on zircon, 1180-1480 m.y.	Post-Mayumbe orogeny and granites: Pb/ $\alpha$ results on zircon, 1250 m.y.	Orogeny and granites: Pb/ $\alpha$ results or zircon, 1466 m.y. and conventional age 1710 m.y.	Unconformity
Mayumbe system: .....	Complexe métamorphique du Mayumbe:	Système de l'Ogooué (in part) includ- ing Série de la Mitendi (1710 m.y.)	Série de Mbalmeyo-Bengis
Série de la Duizi (Série d'Inga included) .....	Série de la Loukoulou		
Disconformity + (?) .....	Disconformity		
Complexe de roches vertes de Gangila and serie de Tshela .....	Série de la Bikossi		
Série de Matadi-Palabala .....	Série de la Loeme		
Conglomerat de Yalala .....			
Couches de Matadi .....			
Couches de Palabala .....			
	Locally, in the north of this area, un- conformity(?), † various meta- morphic rocks, and "complexe à pyroxènes"	Orogeny and granites $\pm 2500$ m.y.†	Orogeny and granites, $\pm 2500$ m.y.†
		Schists, gneiss, pyroxenic complex (char- nockite complex)	"Complexe de Base," schists, gneiss, complexe calcaire-magnésien (charnockites)

\* All these series are traversed by doleritic rocks that are generally considered to be connected with the lavas linked with the tillitic complexes lying above.

† The distinction between "complexe de Base" and younger rocks is clearer in the north (south Cameroons, northernmost Gabon) than in the south.

rocks further north generally considered to be equivalent to the Mayumbe belt might well be the same age.

*The 660-m.y. age group.* This group is represented by four common lead model ages (galenas from a Cu, Pb, Zn, mineralization with Fe, As, Sb, Ag, Au, and locally some Co and U in the Niari area of the Congo Republic and in the Republic of Congo). (The same mineralization also occurs in northern Angola, but no geochronological results have been obtained.) This mineralization, in part stratiform, is linked at least in part with important faults cutting through the Schisto-calcaire and Schisto-gréseux Systems. At Bamba Kilenda (Republic of Congo) the faults are younger than the upper portion of the *Série de l'Inkisi* and the mineralization is located in the same formation and in the faults themselves.

These faults belong to a riftlike structure in the foreland of the belt. This structure postdates some slight nodulations in the Schisto-gréseux and Schisto-calcaire Systems.

A zircon from what is probably the youngest granite in the du Chaillu massif has a lead-alpha apparent age of 630 m.y. (Roques, 1956) that might indicate that this granite belongs to the same age group as the galena leads.

*The 475-m.y. age group.* A group of Ar-K determinations carried out on biotites (and feldspar) from Republic of Congo yield homogeneous results ranging from 446 to 510 m.y. that can be expressed as  $475 \pm 35$  m.y. (Hurley, 1958). The minerals tested come from pegmatites and schists near Boma, pegmatites near Matadi, and Lufu granite near Inga. All these rocks are emplaced in the Mayumbe belt.

It is worth noting that zircon from two facies of the Lufu granite near Inga gave lead-alpha apparent ages of 1180 and 1480 m.y., whereas the biotite from the same granite yields  $475 \pm 35$  m.y.

This metamorphism of the biotite of the relatively old Mayumbe orogenic belt is interpreted as caused by the action of the post-Schisto-gréseux orogeny that seems to have been extremely potent. Beds belonging to the older Mayumbe belt have been overturned or thrust upon younger beds that have been involved only in the post-Schisto-gréseux orogeny. One of the structures involved is the Matadi anticline through which cuts the posttectonic Noqui-Sohio riebeckite-aegyrine granite. This granite therefore postdates the post-Schisto-gréseux orogeny (L. Cahen and P. Thonnart, unpublished observations).

*The 350-m.y. age group.* This group is represented by a homogeneous group of five galena leads in the lower Republic of Congo and in the Congo Republic, the model ages of which range from 310 to 380 m.y. (Eberhardt, unpublished observations). This mineralization seems quite distinct from the older 660-m.y. mineralization that contains ores of numerous metals. The younger mineralization is limited to silver-rich galena.

### Summary

In this west coastal area of equatorial Africa three successive belts have been approximately dated. The oldest, known as the Complexe de base or Basement Complex, occurs in Gabon and the southern Cameroons. It com-

prises micaschists, gneiss, and charnockitic rocks and is approximately dated at 2500 m.y. or older. In the southern portion of the area under review, this early belt is succeeded by the Mayumbe belt several thousand meters thick that runs parallel to the coast from northern Angola through the lower Republic of Congo to the Congo Republic. It is composed chiefly of micaschists, mica-quartzites, graphite, chlorite- and sericite-schists with interstratified uralitized lavas, and syntectonic granites and other intrusives roughly dated by the lead-alpha method on zircon.\* The age is likely to be older than 1480 m.y. and might be of the order of 1750 m.y.

In the same area, this belt is succeeded by another, the remnants of which are situated slightly to the west. It comprises a great variety of rocks ranging from slightly metamorphic to nonmetamorphic. These rocks, about 6000 m. thick, are classified in a certain number of systems, and in the Republic of Congo are known collectively as the Groupe du Congo occidental. The orogeny, which gave this belt its individuality, is known as the post-Schisto-gréseux orogeny (TABLE 3). Two episodes of this orogeny seem to have been dated.

A mineralization located in a riftlike structure in the foreland of the belt may be about 660 m.y. old, whereas the metamorphism in or near the axis of the belt is  $475 \pm 35$  m.y.

The two last events in the area are the intrusion of the Noqui-Sohio riebeckite-aegyrine granite and a new lead mineralization of about 350 m.y.

No rocks of certain Paleozoic age are known. All rocks of above-mentioned formations are earlier than the lead mineralization dated at about 660 m.y. Although they contain stromatolites and certain *Girvanella*-like microfossils, no recognizable fossil of stratigraphic value has ever been found, despite thorough searching.†

The oldest fossiliferous formations that cover these ancient rocks belong to the Mesozoic; they have suffered no orogenesis.

#### WEST AFRICA

A certain number of age determinations have been obtained from the following countries of this area: Guinea, Sierra Leone, Ivory Coast, Ghana, Togo, Dahomey, Nigeria, and the northern part of Cameroons. TABLE 5 gives the general succession in four of the best-known areas.

#### Geology

The geology of Liberia between Sierra Leone and the Ivory Coast is very little known, thus correlation of the succession of the former country with that of the others is extremely tentative. The main discussion is centered around the stratigraphical position of the Akwapimian of Ghana and Atacorien of Dahomey that, in part or whole, represent the same series. By some French

\* These zircons are unlikely to be inherited as they are distributed in rocks of various nature and origin over a very large area. The metamorphism of these rocks is, in part at least, due to the second, post-Schisto-gréseux orogeny.

† Unpublished results obtained later allow another interpretation. The lead with a conventional age of 660 m.y. might be originally syngenetic at the top of the Schisto-calcaire and locally reworked during the post-Schisto-gréseux tectonic episode. If this is the case, the Schisto-gréseux rocks would be younger than 660 m.y.

geologists the Atacorien is considered to be pre-Birimian, whereas by others and by Ghana geologists it is thought to be post-Birimian.

In Nigeria, a "basement complex" of schists, phyllites, quartzites, marble, gneiss, and migmatites is invaded by two groups of granites: widespread "older granites" with pegmatites, and the well-known "younger granites" more restricted in distribution.

### Geochronology

A body of work has been done, but it does not throw much light on the entire succession. Four age groups can be distinguished:

(1) Minerals from pegmatites and veins associated with synkinematic granite in the Sula (Kambui) schists of Sierra Leone. This homogeneous group comprises a  $Pb^{207}/Pb^{206}$  age on monazite and three common lead model ages. The

TABLE 5  
GENERAL SUCCESSION IN FOUR OF THE BEST-KNOWN AREAS

(1) Sierra Leone (Pollet, 1951)	(2) Ivory Coast (Marvier, 1953)	(3) Ghana (Junner, 1946)	(4) Dahomey (Pougnet, 1957)
		A	B
Rokell River series	Falemien	Buem Akwapimian + Togo	Buem
Granites	Tarkwaian	Pegmatites Tarkwaian Granites	Granite
Marampa schistes Granites	Birimien	Birimian	Atacorien
Kambui schists Granites	* Dahomeyen	Migmatites Dahomeyan	Migmatites
Kasila series			Dahomeyan

\* Succession is tentative.

former is  $2940 \pm 200$  m.y. (Wilson *et al.*, 1954), the latter range from 2890 to 3020 m.y., and the average  $2955 \pm 125$  m.y. (Wilson *et al.*, 1954; Eberhardt *et al.*, 1956). An age limit of ca. 2950 m.y. is therefore feasible for these schists, which are generally correlated with the Dahomeyan.

(2) Five model ages on leads from galena in post-Birimian and pre-Tarkwaian gold reefs in Ivory Coast and Guinea show the narrow range of 2160 to 2220 m.y. and average  $2190 \pm 100$  m.y. (Eberhardt *et al.*, 1956). They may be compared (see under **Concluding Remarks**) to not very discordant results on uraninite from the Grabo pegmatite that intrudes schists attributed to the Birimian. The  $Pb^{207}/Pb^{206}$  apparent age is  $1960 \pm 20$  m.y. The other apparent ages range from 1710 to 1820 m.y. (Bernazeaud and Grimberty, 1956). It therefore seems certain that the Birimian rocks are older than about 2000 m.y. Two apparent ages are worth putting on record, although they must be confirmed before conclusions may be drawn. The first is a lead-alpha age of 2640 m.y. (Roques, 1956) on zircon from the Man charnockite that is attributed to the Birimian. This apparent age is comparable to that obtained

by the same method on charnockites of northern Gabon and southern Cameroons (2500 m.y.). A single Ar-K result on feldspar of a post-Tarkwaian pegmatite at Konongo yielded 1645 m.y. (Holmes and Cahen, 1955, 1956).

(3) A group of eleven common lead model ages yield an average conventional age of 590 m.y.; they all fall in the range  $580 \pm 180$  or, if the extremes are omitted,  $625 \pm 95$  m.y. (Eberhardt *et al.*, 1956; Horne, 1960; Holmes and Cahen, 1957).

These model ages are unsupported by data based on other methods. However, the widespread occurrence of these galena leads (Nigeria, Togo, southern Sahara, and northern Cameroons) seem to indicate that at that time an important lead mineralization was introduced.

Most of these conventional ages are measured on lead from galenas that, in all probability, have migrated to their present position (post-Albian lead mineralization of Nigeria and younger granite of 157 m.y. old). However, certain of these galenas, in granites ("granites ultimes") of northern Cameroons for example, which may form part of the older granite suite of Nigeria, may approximately date these granites.

In this connection it may be worth mentioning the Rb-Sr apparent age of 475 m.y. on mica from the Dogon Daji pegmatite in Nigeria. This pegmatite is considered to be linked with the "older granite." An alluvial monazite yielding discordant ages and supposed to stem from the younger granite has a  $Pb^{207}/Pb^{206}$  age of 485 m.y. The other apparent ages range from 245 m.y. to 365 m.y. (Schürmann *et al.*, 1955).

(4) A group of young ages, two of which are relatively precise, characterize the younger granite suite of Nigeria. The best of these ages is obtained on fergusonite and lead to  $157 \pm 25$  m.y. (Darnley, article in press). The younger granite therefore belongs to the Mesozoic.

### Summary

Of the various formations of west Africa only the younger granite and the Kambui (Sula Mountains) schists can at present be considered to be dated with some precision.

Data concerning the Birrimian are also of value. The indications concerning other formations are as yet very limited.

### NORTHERN AFRICA

Only a very few age determinations have been carried out on the minerals and rocks of northern Africa. One or two results have been obtained from the western side of the Sahara Desert. Until recently the eastern side was not much richer. However a body of work on rocks from Egypt is being undertaken, and the first results have just been made known (Gheith *et al.*, 1959).

### Geology

Two Pre-Cambrian successions are of interest in connection with the few age determinations known at present. They are summarized in TABLE 6. No correlation between the two columns is intended.



## Geochronology

*Morocco and Spanish Sahara.* Mica from a pegmatite accompanying the last granitic rocks in Pre-Cambrian I of Morocco yields by Ar-K an apparent age of 1655 m.y. (obtained by H. A. Shillibeer and K. Watson, reported by Holmes and Cahen, 1955, 1957).

This recalls a reported age of  $1750 \pm 150$  m.y. on fuchsite from gneiss of Bulautad area, Spanish Sahara. These gneisses are attributed to the "Lower Pre-Cambrian" (Mingarro and Arribas, 1956). However, the physical constants used are not reported, and this comparison therefore may not be valid.

*Egypt.* Ten Ar-K age determinations on biotite and feldspar from granites and gneisses believed to be of different geological age yield apparent ages falling into what appear to be two age groups.

TABLE 6

Morocco (Choubert, 1952)	Egypt (see Gheith <i>et al.</i> , 1959)	
Lower Cambrian	Gattarian granites	
Adoudounian unconformity	Eparchean	Hamamat series unconformity
Pre-Cambrian III mainly volcanics (some organic remains) unconformity granites		Dokhan series with plutonic rocks similar to Gattarian
		Shadli series
		Series of old paraschists unconformity
Pre-Cambrian II organic remains, Algae and (?) Protozoans unconformity granites	Shaitian granites	
	Metar- chean	Atalla series Mitig series
Pre-Cambrian I	Protar- chean	Feiran series

The older group consists of one determination yielding a "preliminary age" of 625 m.y. (Hurley *et al.*, 1958) on Dara granite, Wadi Hawaishia, Eastern Desert. This granite belongs to the Gattarian granites.

The younger group comprises eight determinations yielding provisional ages between 435 m.y. and 540 m.y. (Gheith *et al.*, 1959; Schürmann *et al.*, 1957). Another result (308 m.y.) is undependable. Whether this group can be considered as representing one event occurring at say, 485 m.y. or whether all or part of the 105-m.y. spread is real is still uncertain.

Most of the biotite and the feldspars have been separated from Gattarian rocks. However, two are believed to be of Protarchean age, and one of Metarchean or very early Eparchean age. The evidence indicates "possibility of recrystallization during the Gattarian time" (Gheith *et al.*, 1959). It is worth noting that the possibly 625-m.y.-old "Gattarian" Dara granite is at least 200 km. to the north of the apparently younger "Gattarian" granites.

These results are quite comparable to those obtained in Kenya, for example, as discussed earlier.

It appears that the late Pre-Cambrian and early Paleozoic activity that characterize the Mozambique belt can be traced farther north along the same general trend.

### Concluding Remarks

#### SUMMARY AND GEOCHRONOLOGICAL USE OF COMMON LEAD-ISOTOPE ANALYSES IN MIDDLE AFRICA

The general picture presented by geochronological work in middle Africa is that of relatively dispersed and scattered work. In northern Africa very little has been done.

The reasons for this state of things are easy to understand: partition of this vast area in numerous political entities; until recently, only very slow comprehension by most geologists of the role and possibilities of geochronology; until more recently still, lack of appropriate tools to carry out the age determinations.

Most of the work in middle Africa has been carried out with one main objective: to obtain an over-all picture of the succession of the most important Pre-Cambrian formations in order to ensure stability of the stratigraphical column, and most of the material collected stems from areas that geologically were considered to be homogeneous.

To date, this objective has met with a certain measure of success, and the approximate age of quite a number of ancient orogenic belts has been ascertained. Against this asset, there are liabilities: with one or two exceptions (FIGURE 2), none of these belts can be considered securely dated although the order of magnitude of the age and the order of succession of number of these belts is known. Large stretches of ancient rocks remain as yet undated.

This first phase of work is now gradually being superseded by more systematic programs designed to yield results as definitive as possible in each belt.

Owing to the insecure status of the Ar-K and Rb-Sr methods at the time when much of the work at present available was undertaken, a large number of galena leads were analyzed in order to supplement the information based on the not-too-frequent uranium minerals.

As the limitations of the geochronological interpretation of common lead-isotope analyses are well known it is worthwhile showing, in the following paragraphs, to what extent reliance has been placed on these results.

Of the numerous existing common lead-isotope analyses only a certain number have been selected for use in this paper.

It is well known that typically anomalous leads exist. Criteria have been devised for their detection (Eberhardt *et al.*, 1955; Cahen *et al.*, 1958). It is not so easy to detect normal leads that have or may have migrated from their original geological position to a new environment. These leads are of course devoid of geochronological significance relatively to the present host rocks. It appears that in a given area those galenas that are relatively poor in silver content and in trace elements are likely to have been formed, whether com-

pletely or partially, of migrated lead (Cahen *et al.*, 1958). Both these categories have been eliminated as far as possible.

Isolated galenas with leads of apparently normal isotopic constitution have also been neglected except when their model age is supported by outside geochronological evidence.

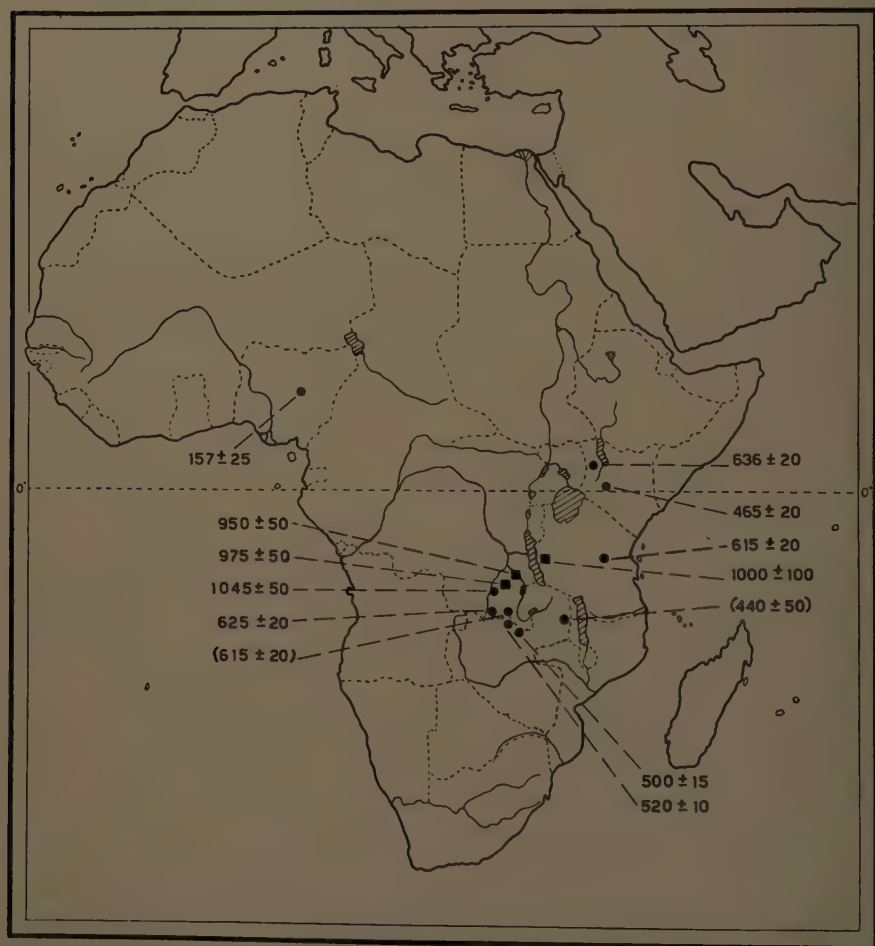


FIGURE 2. Reliable age determinations: ●, concordant uranium lead results; ■, concordant Ar-K and Rb-Sr results.

In these circumstances, in each belt from which a certain number of common lead analyses have been obtained, the majority of these analyses can be united in a relatively homogeneous group, the constitution of which characterizes the belt. Frequently outside this group other leads show an isotopic constitution characteristic of that of a younger belt that generally is marginal to the older one. This is not surprising, as the veins containing these galenas can naturally be very much younger than the rocks they traverse.

The following paragraphs give the characteristic isotopic constitution of lead from galenas from several belts that are more or less precisely dated by other geochronological evidence.

### *Katangan Belt*

Five analyses from Katanga proper are contained between the following limits:

$$18.15^{+0.14}_{-0.11}; \quad 15.76^{+0.04}_{-0.09}; \quad 38.06^{+0.17}_{-0.20}.$$

Average of the conventional ages: Holmes-Houtermans model, 528 m.y.; Toronto model, 439 m.y.

Other geochronological evidence:  $625 \pm 20$  m.y. and  $520 \pm 20$  m.y.

### *Kibara-Urundi-Karagwe-Ankolean Belt*

Next to some galenas with lead similar to that of the Katangan belt, four galenas may be characterized thus:

$$17.69^{+0.07}_{-0.13}; \quad 15.80^{+0.08}_{-0.04}; \quad 37.46^{+0.15}_{-1.18}.$$

Average of the four model ages: Holmes-Houtermans model, 896 m.y.; Toronto model, 705 m.y.

Other geochronological evidence:  $1000 \pm 50$  m.y.

### *Ubendian-Ruzizi Belt*

One galena lead follows the Kibaran pattern; two others yield the following average:

$$16.42^{+0.00}_{\pm 0.00}; \quad 15.59^{+0.02}_{-0.02}; \quad 36.91^{+0.19}_{-0.20}.$$

Average model age: Holmes-Houtermans model, 1565 m.y.; Toronto model, 1163 m.y.

Other geochronological evidence: order of 1600 m.y.

### *Kibalian Belt*

Two galena leads yield the following average:

$$15.92^{+0.19}_{-0.19}; \quad 15.52^{+0.03}_{-0.02}; \quad 35.77^{+0.04}_{-0.04}.$$

Average model age: Holmes-Houtermans model, 1840 m.y.; Toronto model, 1540 m.y.

Other geochronological evidence: (correlation with Buganda schists)  $1855 \pm 10$  per cent m.y.

### *Birimian Belt*

Five galena leads average:

$$15.08^{+0.30}_{-0.24}; \quad 15.25^{+0.23}_{-0.18}; \quad 35.03^{+0.58}_{-0.31}.$$

Average of the five model ages: Holmes-Houtermans model, 2190 m.y.; Toronto model, 1900 m.y.

Other geochronological evidence (correlation): 1960 m.y.

### *Sula Mountain Schists*

Three galena leads are comprised in the following limits:

$$13.69^{+0.32}_{-0.19}; \quad 14.91^{+0.24}_{-0.13}; \quad 33.78^{+0.59}_{-0.36}.$$

Average of the three model ages: Holmes-Houtermans model 2966 m.y.;  
Toronto model, 2465 m.y.

Other geochronological evidence:  $2940 \pm 200$  m.y.

*Ancient Formations of North Congo (Gangu Group)*

Two galenas (three analyses) yield:

$$12.70 \begin{smallmatrix} +0.04 \\ -0.07 \end{smallmatrix}; \quad 14.34 \begin{smallmatrix} +0.04 \\ -0.02 \end{smallmatrix}; \quad 32.66 \begin{smallmatrix} +0.05 \\ -0.05 \end{smallmatrix}.$$

Average of the three model ages: Holmes-Houtermans model, 3380 m.y.;  
Toronto, 2910 m.y.

Concerning other geochronological evidence, there is no local evidence; these leads are, however, practically identical to the well-known Rosetta Mine lead, the great antiquity of which is substantiated by two or three very ancient ages (over 3000 m.y.) in similar formations in the same general area.

The above evidence shows that after elimination of a certain number of unreliable leads: (1) the isotopic constitutions of lead ores in a given belt are characteristic of the belt (this is distinct from the mode of computation of the model age); and (2) where geological superposition between belts has been observed, the order of the isotopic ratios  $\text{Pb}^{206}/\text{Pb}^{204}$ ,  $\text{Pb}^{207}/\text{Pb}^{204}$  and  $\text{Pb}^{208}/\text{Pb}^{204}$  is in accordance with geological evidence.

It therefore seems possible, providing inappropriate specimens are eliminated, to use the isotopic composition of a sufficiently homogeneous group of lead ores as a kind of "fossil."

(3) In middle Africa, the ages computed from the isotopic ratios following the Holmes-Houtermans model are reasonably good approximations of the ages obtained by other more reliable geochronological methods. The approximation of the Toronto model is generally not so good. One instance where the contrary may be the case is that of the five post-Birimian ores of west Africa, averaging 2190 m.y. using the Holmes-Houtermans model and 1900 m.y. using the Toronto model. Latter model age compares better with the best age of the uraninite of Grabo pegmatite (1960 m.y.) that cuts through rocks attributed to the Birimian.

RELATIONSHIP AND DISTRIBUTION ON THE AFRICAN CONTINENT OF "YOUNG"  
AGES OF THE 475 TO 650 M.Y. ORDER OF MAGNITUDE: THEIR BEARING  
ON THE PROBLEM OF THE CAMBRIAN—PRE-CAMBRIAN LIMIT

*Relationship Between Ages in the "475 to 650-m.y." Range\**

In previous publications (Holmes and Cahen, 1955, 1957), "Katangan" ages of about 625 m.y. and "early Cambrian" ages of 485 m.y. were considered to belong to distinct cycles of activity.

The occurrence and distribution of reliable ages in this time range tends to a revision of this idea.

In the Katanga and Rhodesia copper belt concordant ages on uranium minerals range from 500 to 625 m.y.

In the northern portions of the "Mozambique belt" in Kenya and Tanganyika, the range is 485 to 636 m.y.

\* Some comments on this subject have been published, quite independently, by Holmes (1960).



In lower Congo, apparent ages (Ar-K) in the range  $475 \pm 30$  m.y. coexist with model ages of  $660 \pm 40$  m.y.; in addition younger model ages ( $350 \pm 40$  m.y.) are also present.

In west Africa there is also evidence of the coexistence of ages in the 475-m.y. range with model ages in the 600-m.y. range. Apparent ages by the Ar-K method from Egyptian rocks also show the same range.

This situation is also known in other parts of Africa, including Nyassaland, Mozambique, and Madagascar.

In the present state of knowledge it appears that these spatially-linked ages may represent different episodes in a more or less continuous evolution.

In certain areas, where the geological history has been more or less adequately unraveled, this does appear to be the case, as discussed earlier.

*Distribution of Ages in the "475 to 650-m.y." Range*

The classical picture of the African continent follows. Most of the inner portion of Africa consists of a Pre-Cambrian basement unconformably overlain by flat-lying or very slightly folded continental beds of Upper Carboniferous age and younger. Fold belts of post-Pre-Cambrian age are known in the extreme south (Cape folding) and in the north (Atlas Mountain range). Flat-lying or slightly folded Lower Paleozoic beds are known inland over quite an important part of northern Africa, but only in a very few patches in southern Africa.

Geochronology is rapidly modifying this picture, and Lower Paleozoic ages are turning up in many quarters, not to mention the Mesozoic ages recently found for the Nigerian younger granite.

It is of interest to point out that the ages in the "475 to 650-m.y." range, although they occur in several parts of interior Africa, are also found along almost all the coast of the southern part of Africa and also along the eastern coast of the northern part of the continent.

Along the west coast these ages are more or less directly linked with formations known or believed to belong to the end of the Pre-Cambrian: Groupe du Congo occidental in Gabon, Congo Republic, Lower Congo, and Angola; Otavi and Damara of southwest Africa; and Malmesbury series (South Africa). Over most of this stretch, these formations have trends approximately parallel to the present coast line. These ages are found not only in formations of late Pre-Cambrian age but also in much older rocks that have been influenced by the younger orogeny.

Along the east coast, the situation is or may be different. A long belt, collectively known as the Mozambique belt (Holmes, 1951), spreads through Mozambique, Nyassaland, Tanganyika, and Kenya; its trend is generally north to south roughly parallel to the coast. In northern Kenya this belt disappears under young volcanics in Abyssinia, apparently to emerge again in Sudan and the United Arab Republic (UAR). All along this distance of several thousands of kilometers, no reliable age older than about 650 m.y. has been found in this belt, from which ages of "475 to 650" m.y. are repeatedly produced.

Nevertheless, this belt of high metamorphism has generally been considered to be old, and, indeed, in Madagascar a belt of similar lithology, metamorphism,

and trend (Système du Graphite) appears to be old. Nevertheless there also, quite a number of dated granites and pegmatites fall into the above-mentioned range.

In Egypt the ages in this time range apparently characterize the youngest episodes of a very long sequence of events involving two or more unconformities, at least to suites of granites.

It seems therefore quite possible that, despite its "young" age determinations, the Mozambique belt may be a multicyclic belt in which ancient rocks belonging to older cycles have been reinvolved in a "young" end-Pre-Cambrian to early Paleozoic activity.

Referring to the recently revised time scale (Kulp, 1959; Holmes, 1960), the last important phases of this activity are, in different areas: Cambrian or somewhat later (north Rhodesia and southeast Katanga), early or mid-Ordovician (Kenya, Madagascar, and lower Congo) and end-Ordovician (southern Rhodesia). Galena leads in Lower Congo appear to be about end-Devonian.

The distribution of this activity (FIGURE 3) implies that, toward the close of the Pre-Cambrian and the beginning of the Paleozoic, geosynclinal belts coincided approximately with the present margins of Africa that, with perhaps a part of Asia Minor, was then surrounded by oceans, even if this implied only narrow stretches of oceans. Other branches of this belt are known in the interior of the continent.

It is remarkable, however, that fossiliferous Lower Paleozoic (Cambrian to Ordovician) rocks are, with very few exceptions, absent from Africa south of the Sahara. This may be readily explained in those cases where high-grade metamorphism would in any case have obliterated any fossil remains. In other areas, however, the youngest sedimentary rocks, at present recognized as having been involved in these belts, are cryptozoic, and, in some cases available geochronological data show them to be older than about 625 m.y., as discussed below.

In this connection it should be recalled that the margin of the continent and a number of inland areas have been repeatedly uplifted, at least since Mesozoic times and probably earlier. Even a moderate rate of uplift is compatible with the removal through erosion of many thousands of meters of such fossiliferous rocks; some of these end-Pre-Cambrian, early Paleozoic belt areas may therefore perhaps be considered as roots of these belts. Debris resulting from the postulated erosion would have to be searched for in depressed areas such as inland basins, rift valleys, or under the ocean.

#### *Bearing on the Problems of the Cambrian—Pre-Cambrian Limit*

As a consequence of the development of new methods and of a vast increase in the number of rocks and minerals being dated, the geological time scale is currently undergoing revision.

One of the major problems remains that of the Cambrian—Pre-Cambrian boundary. There are two aspects to this problem: one is the choice of the boundary; the other is the dating of this boundary.

Except perhaps in Morocco, where a richly fossiliferous Lower Cambrian with volcanics is conformably underlain by a thick sedimentary series also

with volcanics that in turn rest unconformably on the "Pre-Cambrian III," it seems unlikely that very precise contributions to these problems should originate in Africa.

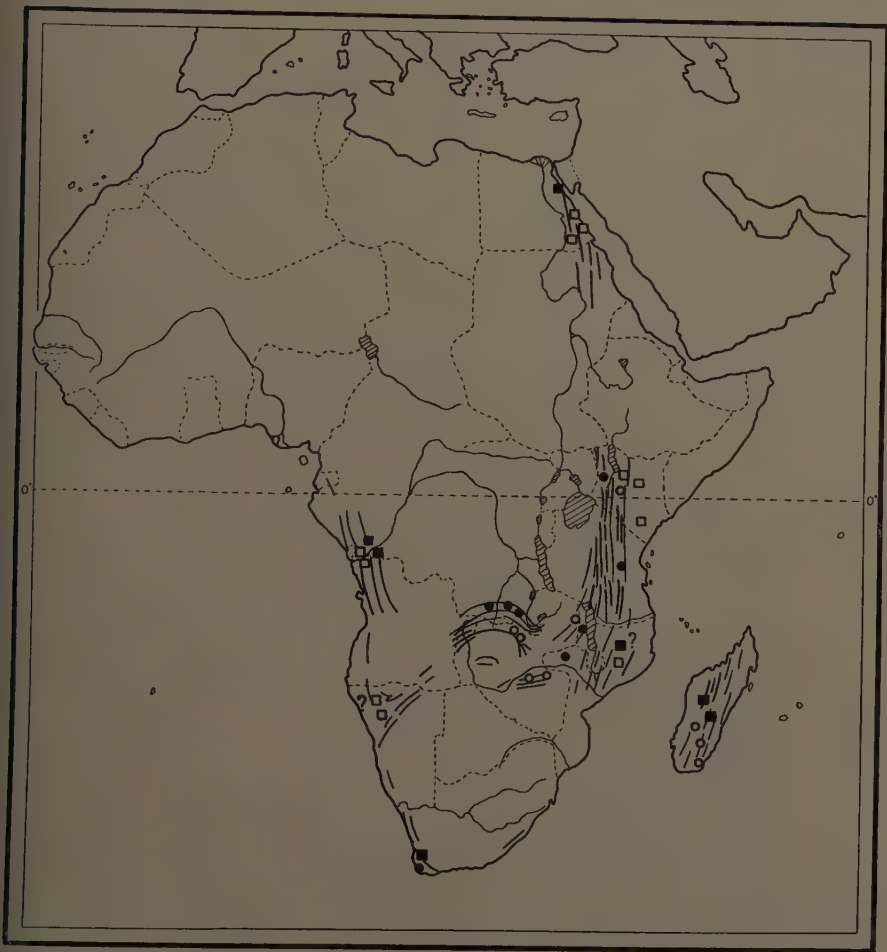


FIGURE 3. Sketch of areas of late Pre-Cambrian-early Paleozoic activity: ○, U-Pb ages under 550 m.y.; □, Ar-K and Rb-Sr ages under 550 m.y.; ●, U-Pb ages over 550 m.y.; ■, Ar-K and Rb-Sr ages over 550 m.y.

There are numerous precise Lower Paleozoic and Upper Pre-Cambrian ages, but there are no fossiliferous sediments linked with them. For example, concordant ages of 485, 500, 520, 565, 584, 625, and 636 m.y. are known in various parts of Africa. Also in some instances two or more of these excellent ages appear in a limited area.

A good example of these occurrences is the Katanga-northern Rhodesia succession.

In this area the "Système du Kundelungu" is entirely or almost entirely older

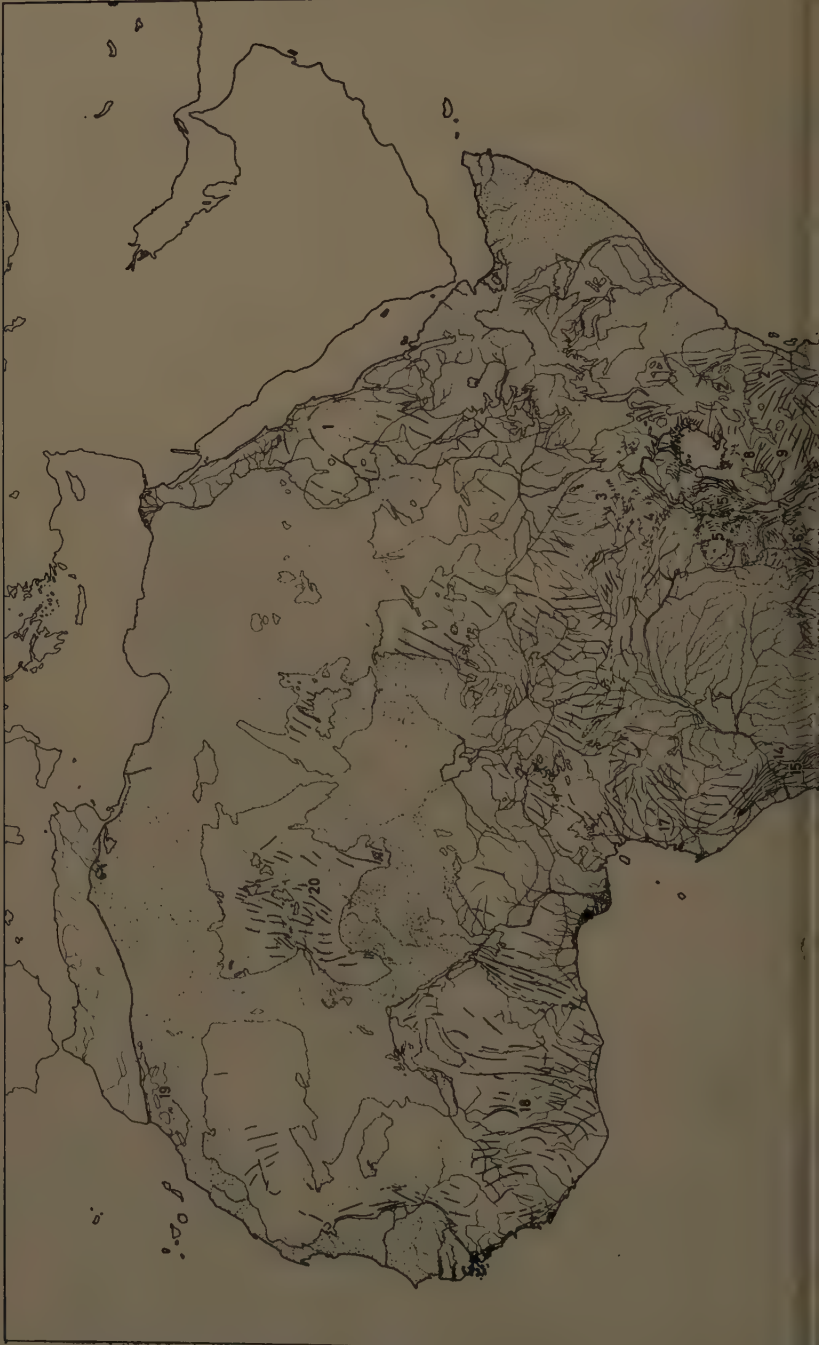




FIGURE 4. Structural sketch of middle and northern Africa. In equatorial Africa the trends have been taken chiefly from original documents; in west and northern Africa, from R. Furon, *Esquisse structurale provisoire de l'Afrique*, Paris (1959), Assoc. Serv. géol. africains.

(1) Egypt and Sudan. Last events of a polycyclic evolution have been dated in Egypt (435 to 540 m.y.).

(2) Mozambique belt. Last events of a possibly polycyclic evolution have been dated (465 to 656 m.y.).

(3) West Nile belt. Considered extremely old; probably older than circa 3400 m.y.

(4) Groupe du Kibali. Probably older than circa 1850 m.y. and probably linked with Buganda series to the north of Lake Victoria, which are certainly older than 1850 m.y.

(5) Groupe de l'Urundi and Karagwe-Akoleian system, imprecisely dated but in physical continuity with No. 6.

(6) Groupe des Kibara. Late orogenic events are dated at  $1000 \pm 50$  m.y.

(7) Ubendian; Groupe de la Ruzizi. Postorogenic phase is dated at circa 1600 m.y.

(8) Nyanzian and Kavirondian. Common lead model ages which may date the Nyanzian are circa 2800 m.y.

(9) Dodoman. Older than 2250 to 2440 m.y.

(10) Katangan belt. Late orogenic uranium mineralization (Shinkolobwe) at 625 m.y., postorogenic uranium mineralization (N. Rhodesia) at 500 m.y.

(11) Irumi belt undated, pre-Katangan.

(12) Rufunza belt, older than Irumi.

(13) Mafingi belt, probably part of the Late Pre-Cambrian-Early Paleozoic activity. One age circa 440 m.y.

(14) Groupe du Congo Occidental. Activity at circa 660 and circa 475 m.y.

(15) Groupe des Monts de Cristal (Système du Mayumbe): older than circa 1500 m.y.

(16) So-called Basement of Northern Angola. Some of this belongs to the Système du Mayumbe (see No. 15). Other crystalline rocks are or may be much younger.

(17) Basement Complex of North Gabon and Southern Cameroons, circa 2550 m.y. or older.

(18) West Africa; see text.

(19) Anti-Atlas-Morocco. One age postdates the earliest Pre-Cambrian in this area, 1650 m.y.

(20) Hoggar. Undated area, generally correlated with the west African section.



than the major thrusts that in turn are postdated by the uranium mineralization of 625 m.y. This mineralization is obviously linked with the last phases of the orogeny, earlier phases of which were concomitant with the sedimentation of the lower and middle Kundelungu beds. There is therefore every reason to believe that the sediments are not very much older than the mineralization. In the different subdivisions of the Kundelungu, there are limestones, shales, and other rocks that, if Paleozoic or younger, normally should prove fossiliferous; indeed most of the carbonate rocks contain stromatolites and some chert horizons contain microfossils (such as protozoans and algae) strongly suggestive of late Pre-Cambrian fossils the world over. There is no trace of a Cambrian fauna, although many gray and greenish shales, if these rocks were Cambrian, should have yielded fossils. It therefore seems that it is improbable that the base of the Cambrian is much earlier than about 625 m.y.\*

A similar conclusion is reached if the lower Congo is considered. An important phase of the post Schisto-gréseux orogeny is dated at about  $475 \pm 30$  m.y., certainly a Paleozoic date. However, all preserved formations are likely to be earlier than a common lead model age of about 660 m.y. These rocks are almost devoid of organic remains. Only stromatolites and some *Girvanella*-like and other micro-organisms can be mentioned.

However, both Katanga and the lower Congo are well-studied regions where numerous geologists have been and still are active. In both these areas the attention of geologists has repeatedly been drawn to the necessity of searching for fossils. Nothing better than very poor *problematica* have ever turned up.

Indeed what can best serve as a Cambrian fauna in Africa, south of the Sahara, has been found in the Nama system of South and southwest Africa that rests unconformably on beds attributed to the Malmesbury series. This series, in its type area, appears to be contemporary to the Katanga and lower Congo beds for the age of the syntectonic Cape granite affecting the Malmesbury series is somewhere in the 550- to 610-m.y. range (Nicolaysen, elsewhere in this monograph).

All this evidence, imprecise as it is, tends to show that the Lower Cambrian fauna developed later than 600 to 625 m.y. but not earlier. However, until a precise date for the base of the Cambrian is available, unfossiliferous rocks deposited just before a 600- or 625-m.y. date, should be considered pre-Cambrian(?) rather than Pre-Cambrian.

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\* Argumentation along this line has previously been presented by Davidson (1959) and Holmes (1960).

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### Discussion of the Paper

B. J. GILETTI (*Oxford University, Oxford, England*): Cahen has mentioned that the "older granites" of Nigeria are probably of the order of 500 to 600 million years (m.y.). My associates and I have obtained an age of 520 m.y. on "older granite" by the Rb-Sr method.

G. W. WETHERILL (*Carnegie Institution of Washington, Washington, D.C.*): What indications are there that the rocks you mention that are younger than about 900 m.y. are indeed Pre-Cambrian?

CAHEN: I refer Wetherill to the more detailed account in my written communication. In Katanga and lower Congo there are no fossiliferous Paleozoic beds overlying the sedimentary successions known as the *Groupe du Katanga* and the *Groupe du Congo occidental*, respectively. The former is certainly dated between 1000 and 625 m.y.; the latter is of the same general age.

In Katanga there is reason to believe that the sediments are not very much older than the uranium mineralization. The different subdivisions of this succession contain organic remains comparable to late Pre-Cambrian fossils the world over, but there is nothing resembling a Cambrian fauna.

Indeed, what most resembles a Cambrian fauna in Africa, south of the Sahara,

has been found in the Nama system, which is likely to be younger than the Malmesbury series that, in turn, appears to be contemporary with the Katanga and lower Congo beds.

However, until a precise date for the base of the Cambrian is obtained, all unfossiliferous rocks deposited just before a 600- or 625-m.y. date should be regarded as questionably Pre-Cambrian.



# SUMMARY OF DISCUSSION OF STRATIGRAPHIC AND TECTONIC INTERPRETATION OF CERTAIN AGE MEASUREMENTS IN SOUTHERN AFRICA

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Certain age measurements from southern Africa and Madagascar have been reviewed. The techniques of stable isotope dilution and isotopic analysis of microgram samples have made possible a significant increase in the number of determinations, and some of these have a direct bearing on long-discussed problems in Pre-Cambrian stratigraphy. Perhaps the most important of these problems is the time correlation of Pre-Cambrian systems in various isolated parts of the subcontinent and those measurements that impose restraints on stratigraphic correlations are particularly important. Correlations adopted in the recently-issued 1:1,000,000 Geological Map of the Union of South Africa are pertinent to the discussion here.

In 1948 A. Holmes (1951) made a pioneering attempt at deciphering the highly complex structural history of this region, emphasizing the use of age measurements in unraveling a sequence of ancient orogenic belts. Recent work has indicated that dating of the relatively flat-lying and unmetamorphosed Pre-Cambrian systems is equally important for an understanding of tectonic history. Relationships concerning absolute age, lithology, and tectonic style are also discussed, in a commentary on the southern portion of the Provisional Structural Map of Africa issued by the Association of African Geological Surveys in 1958. Age measurements also have a bearing on theories of continental growth and continental drift; in considering the tectonic framework of Paleozoic sedimentation in southern Africa and Madagascar, it is important that the many age measurements between 450 m.y. and 600 m.y. should be taken into account and correctly interpreted with respect to the Paleozoic time scale.

Some important unsolved problems in the geochronology of southern Africa are delineated.

The research effort that has been focussed on the time scale, that is, the problem of defining maximum and minimum limits for the deposition times of particular Pre-Cambrian systems, has had some degree of success in the Transvaal Province. An attempt at such a time scale is shown in FIGURE 1. This scale is probably valid for February 1960, but drastic modifications may be expected as further critical measurements are made. Such attempts have their greatest value in exposing the major gaps in our knowledge: in this instance, the times of deposition of the Swaziland, Dominion Reef, and Witwatersrand systems. It has been shown that the time of initial crystallization of the uraninite found in conglomerates of the Dominion Reef and Witwatersrand systems is  $3050 \pm 100$  m.y. Conclusive evidence about the deposition times of these systems would be of major significance to theories of the origin of the uraninite.



# TENTATIVE CORRELATION 1960

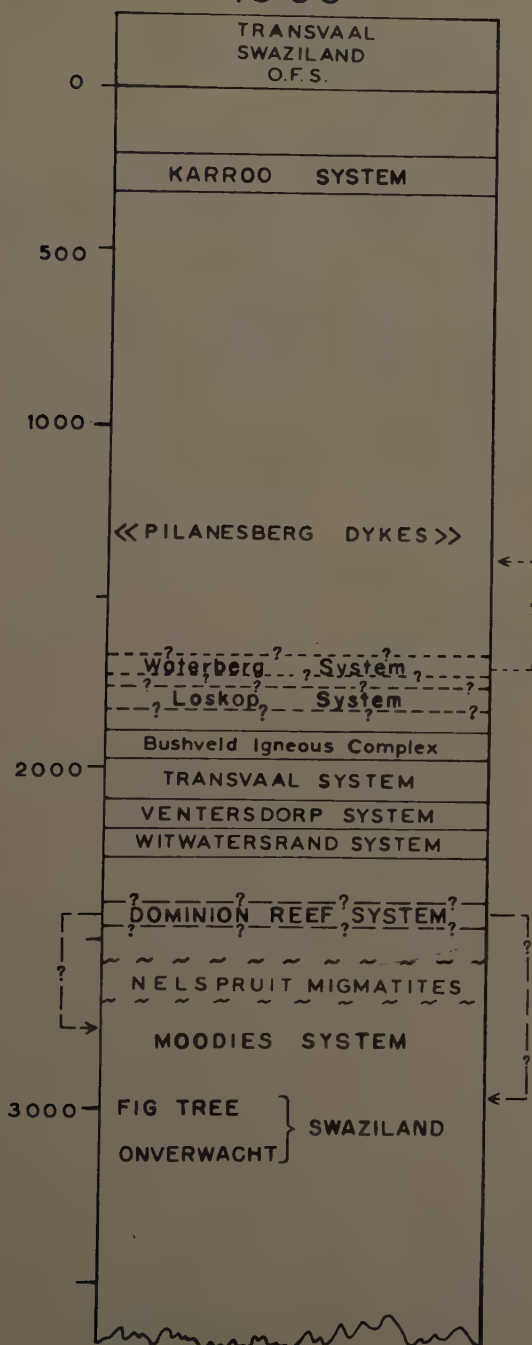


FIGURE 1.

In the region paralleling the Orange River in the northern Cape Province, age measurements have raised new geological problems. There are many age measurements on pegmatites and metamorphic rock of  $\sim 950$  m.y., but it is difficult to construct a time scale for this region in which these plutonic rocks can be related to the stratigraphic column. Holmes postulated the existence of a  $\sim 1000$  m.y. old orogenic belt in this region, but there are no stratigraphic system(s) that can clearly be linked to this hypothetical  $\sim 1000$  m.y. old orogen. There are several analogies between the geochronology and geology of the Marydale-Prieska region and that of the so-called Grenville Front in Ontario and Quebec.

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## Part VII. The Age of the Basement Rocks of the World: Other Areas

### THE BASEMENT OF CENTRAL AND SOUTH AMERICA, OR, HOW NOT TO DATE A CONTINENT

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The basement of Central and South America is such a large area of almost virgin territory that I wonder if perhaps certain geological criteria could not be established that would lessen the work of the geochronologist who is planning to enter such a region. We are beginning to know something about the Precambrian Shield area in Canada, as is clear from C. H. Stockwell's paper in this monograph. However, by analogy, if work were started on this area without any prior knowledge, it would be most unfortunate if the geochronologist were to choose the Sudbury area on which to begin. The investigator would either become discouraged or spend an undue amount of time attempting to make sense of it whereas, if he started elsewhere and approached this area from several directions, he would find that its complexity could be resolved without too much difficulty.

Let us ask, therefore, if there is not some way in which a geochronological study applied to very large region can be substantially aided by planning the sampling program so as to work first on areas that are homogeneous. For example, referring again to the Canadian Shield, it is composed of rather isochronous regions of different ages and, between these regions, both the structure and the age measurements show complexity. A homogeneous region, such as the Superior Province or the Churchill Province, may have been made up initially of numbers of events involving up to tens of millions of years in total age spread. Eventually the area became eroded to sea level. Since the time of peneplanation the area has remained a stable one, as indicated by thin coverings of sediments, and any mineral sample taken from its present surface probably has remained close to that surface since the original time of peneplanation. This fact apparently results in an area of fairly homogeneous age and, although we are not certain that the time of peneplanation was close to the time of the original orogenic developments, at least it is something we can map using current geochronological methods.

If, therefore, the geochronologist hypothetically studying the Canadian Shield area from the beginning had studied samples taken from each structural province in a regular grid, he would have discovered that he could have made an isochronic map of the region in which large plateaulike areas of equal age would be bounded by "noisy" regions before descending to further plateaulike areas of younger age. In this survey, if he were fortunate, it might be possible for him to do the principle reconnaissance of the entire region rather rapidly and, using the knowledge of the bounding areas in each of the so-called noisy areas, he might with relatively few measurements see that these noisy areas were made up of complexes in which the older age was partially residual in the superimposed metamorphism of the neighboring younger belt. This approach would

greatly facilitate his work if it turned out that most Pre-Cambrian regions were predominantly of this kind. If, on the other hand, it turned out that the areas were all noisy, then he would derive no great benefit from such a reconnaissance procedure. However, in examining the other Pre-Cambrian areas of the world, it is beginning to appear that these regions are truly of this nature and that isochronous belts are indeed of major geological significance and should be outlined.

Already it is becoming clear that methods will eventually be worked out with which it will be possible to tell in a simple test whether a plutonic rock is freshly derived from subcrustal regions or whether the rock represents a reworking of some more ancient sialic material. I am thinking in particular of the strontium-87 abundance in the whole rock, calculated back to the time measured in the micas. It is becoming quite apparent that the average mantle abundance of strontium-87 varies only slightly with time, reaching a present value of 0.712. Thus, if a granite shows a strontium-87 abundance of about 0.712 at the time of its emplacement, it is fairly likely to have been derived from the mantle at that time. If, however, as is indicated by the tests on the wall rocks of the 260 million year-pegmatites in the Middletown area in Connecticut or on many of the rocks of the Sudbury region, that the whole-rock strontium-87 abundance is higher than this at the time measured for the intrusive activity, it is quite apparent that this material represents reworked sediments or metamorphic rocks of more ancient vintage. These simple tests may well turn out to be quite diagnostic and establish the validity of the ages measured in any region of homogeneous ages so that the geochronologist can pass on without question to further study elsewhere.

Turning now to the problem of the crystalline basement rocks in Central and South America, my associates and I hope to initiate a program of the kind outlined above. This intent was stated several years ago, but it was found impracticable to obtain samples on any systematic basis from large areas, for obvious reasons. In most cases the regions were not opened up or, if they were, the geological mapping had not extended far enough even in reconnaissance form to establish the fact that basement crystalline rocks were underlying the region. The problem resolved itself into taking samples that were available because of the prohibitive cost of an organized collection program.

We have thus barely made a start on the problem. Through the courtesy of petroleum companies in Colombia and Venezuela we obtained a few samples of basement crystalline rock from drill cores and outcrops. An initial report on these samples and the age measurements that have been made in Colombia has been submitted to the Geological Society of America for publication in the *Bulletin* under the authorship of W. H. Pinson, Jr. (in press).

In summary, four periods of metamorphism or orogeny have been suggested by the age measurements and the geological study of the region as a whole. The western part of the Guayana Shield in the vicinity of the Guaviare River near San José del Guaviare, Colombia, shows an age of approximately 1200 million years (m.y.) by concordant K-Ar and Rb-Sr measurements. The extreme western edge of what was believed to be the Guayana Shield, approaching the Macarena Mountain region east of the main Cordillera in Colombia,

showed a basement age of approximately 450 m.y. by both methods. This is in agreement roughly with a period of folding and tectonism in the Macarena Mountains. In the northwestern corner of the continent, in the area of the Cicuco Oil Field, the basement rock at 8000 feet was found to show an age of approximately 110 m.y., in agreement with Late Nevadan intrusive events in nearby regions. In the northern part of the continent the basement rock from a drill hole several thousand feet in depth into the base of the Maracaibo Basin gave an age of 246 m.y., which is quite similar to the so-called Appalachian ages found in eastern parts of the North American continent.

These two last ages coupled with the known geology of the region suggest that periods of marginal mountain development in the northern part of the South American continent were similar to or extensions of periods of orogenesis or disturbance that affected the North American continent, including the Taconian, the Appalachian, and the Nevadan. Apparently these belts sweep around on either side of the principle Guayana Shield area of Pre-Cambrian age, intermediate belts possibly occurring between the coastal regions and the interior highlands.

Turning now to the principal central shield areas in South America, namely the eastern shield of Brazil and the Matto Grosso shield in the interior, we found that it was possible to obtain samples from the former region only. Also, in order to coordinate the age work with known geological mapping, it was found that the work had to be restricted entirely to the area of the Quadrilatero Ferrifero in Minas Gerais that was being studied intensively by United States Geological Survey Foreign Branch geologists in collaboration with Brazilian geologists. Unfortunately this area turned out to be precisely the type of area that we wished to avoid, as it is similar to the Sudbury area in Ontario.

A detailed report of the geochronological data correlated with the results of the intensive geological study that was carried out in an excellent and thorough fashion by the United States Geological Survey Foreign Branch has been submitted for publication in the *Bulletin of the Geological Society of America* under the authorship of Norman Herz (in press). The geological work at first indicated that there were at least two major orogenic events in the region, but they were believed to be of fairly late Pre-Cambrian age. The age studies subsequently showed measured dates covering the entire range of Pre-Cambrian history as known on other continents.

The oldest measurements at 2500 m.y. correlated with the oldest established rocks in the field, but much complexity appeared in the correlation of other lithologic units with the age values down to the youngest events at approximately 500 m.y. Thus it seems that there are at least two major events in the region, the oldest at 2500 m.y. and the youngest at 500 m.y., with a fair possibility of at least one other superimposed event lying between these limits at approximately 1300 m.y. Without going into further detail it is obvious that the kind of reconnaissance mentioned earlier in this article will be needed to unravel this complexity. It has been recommended that the next program involve a broad sampling in the eastern shield area, as systematically as possible in an even coverage, so that regions of homogeneous ages may be outlined before work is continued on the complex boundary regions. Such work of course



should be coupled with aerial photographic and magnetic data and geological reconnaissance.

From these beginning measurements on South American basement rocks, it is clear that the South American continent is as old as others now are known to be and that a fairly similar system of development is expectable, even extending to the marginal belts along the coasts. In fact, although it is much too early to draw conclusions, it is remarkable that many of the ages observed in North America both in the interior and in the marginal mountain systems seem to have corresponding ages in the initial values found in South America.

#### *Discussion of the Paper*

G. R. TILTON (*Carnegie Institution of Washington, Washington, D.C.*): I am not clear as to whether you are recommending that we stay out of these noisy areas, or whether you mean they should be avoided just for the first preliminary work. Would you clarify this, please?

HURLEY: I certainly believe that the excellent work of the type being carried on at the Department of Terrestrial Magnetism at the Carnegie Institution in attempting to find ways of unscrambling these difficult areas should be maintained. We are doing this also. This kind of work is precisely what is needed at this time and is particularly advantageous in pointing out to geologists that a simple set of age measurements, even if apparently fairly homogeneous, does not necessarily give the correct age for a region. However, if regional geological studies in the Pre-Cambrian are going to be made anyway, the investigators should at least attempt to keep away from the noisy areas if possible, leaving these difficult studies for more intensive work following a general reconnaissance. I am not in favor of applying geochronological techniques as they now stand without a most thorough knowledge of the kinds of problems and difficulties that can be encountered as well as of possible ways by which these problems may be solved. We cannot stop the application of these techniques, but at least we can point out ways in which the work at present can best be performed by those who wish to apply the techniques to actual dating of continental regions.

S. S. GOLDICH (*United States Geological Survey, Washington, D.C.*): An important point has been raised here. I have data on the Snowbank stock in Minnesota, a postkinematic Algoman intrusive complex in a belt of Knife Lake metasediments and one of a number of noisy points in Minnesota. Although it would appear that there were intrusions at 1.0, 1.2, 1.7, and 2.3 billion years, actually the 1.0 billion year date is the Duluth gabbro, and the other numbers probably reflect metamorphism of older rocks by the gabbro.

My thesis is that, combining geological information and even very crude K-Ar studies, these areas can be found. It is not absolutely necessary to solve all these particular problems. We could sit on this for years before going ahead with a broad study of Minnesota and Ontario to make a geological contribution that is really worthwhile.

G. W. WETHERILL (*Carnegie Institution of Washington, Washington, D.C.*): Reference to a recent paper by Gordon Gastil on North American Pre-Cambrian orogenies has been made elsewhere in this monograph, and I feel that

in view of the complexities we have seen in interpreting much of this 1300, 1600, 1700, and 1800 m.y. information, as in North America, I think it would be rather unfortunate if it should become a standard reference at this point.

P. E. DAMON (*University of Arizona, Tucson, Arizona*): This information was used because it was available. However, I shall point out that it is only from the conversations between the geologist and the geochemist and the geophysicist that we are really going to advance.

In a sense, geology represents a control on the geochemical work, as well as vice versa. If the investigator arrives at improbable conclusions, he may suspect that there is something wrong with his crystal chemistry or his dating technique.

L. T. ALDRICH (*Carnegie Institution of Washington, Washington, D.C.*): Returning briefly to South America: my associates and I were in Peru to look at the alto-plano seismically and, of course, I had to collect some rocks while we were there. We collected samples that had the best chance of being the Pre-Cambrian of Peru. The area was simply labeled Pre-Cretaceous, which was all the control that was on it but, since this was all that was available and we were there, we took it. In fact it is Pre-Cretaceous, but this is about all one can say.

J. L. KULP (*Columbia University, New York, N.Y.*): Along the north shore of Venezuela, a green belt is seen that is mapped as Cretaceous and consists of gneisses and schists. There has been much debate as to whether the final activity was Cretaceous or later. My associates and I have obtained mica ages as young as 25 m.y. While clearly this does not establish a 25 m.y. metamorphism, it does show that there was some heating in the later Tertiary. This fact shows that things have not been stable in this area since the Cretaceous and hence has implications for the petroleum geology of the region.

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## THE ABSOLUTE AGES OF EAST ANTARCTIC ROCKS

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In this article we set forth the results of the first phase of our work on absolute dating of Antarctic rocks.

The available information about the geological structure of East Antarctica is very limited.<sup>5,6,7,10,12</sup> The principal obstacle to the study of Antarctic geology is that almost its entire area is covered by a thick blanket of ice. Only scattered outcrops of bedrock are found along the edge of the continent.

If the geological structure of the Antarctic as a whole has received little study, its eastern littoral has been studied least of all. Investigations conducted by geologists of the Soviet Antarctic Expedition during the period 1956 to 1958 have made a substantial contribution to the geology of East Antarctica.<sup>2,5,6,7</sup> However, even if we take these investigations into account, we still have rather fragmentary and schematic ideas about the geological structure, age, and distribution of the rocks that make up the Antarctic shield.

All the territory that has been examined is part of the East Antarctica platform, which has a three-layered structure and is similar in some respects to other Gondwana platforms. The lowermost structural layer is composed of various gneisses and schists, among which migmatites and granitoids of ultra-metamorphic origin are extensively distributed. In this layer we find strongly metamorphosed basic intrusions transformed into pyroxenites and amphibolites. Massifs of hypersthene granites of the charnockite-mangerite series are abundant. Massifs of porphyroblastic granite gneisses, Rapakivi granites, and aplitic granites are found less often. Infrequent intrusions of subalkaline biotite-hornblende granites are of more recent origin.

The middle structural layer is composed of chlorite-epidote schists, and phyllites of the green-schist facies of metamorphism, as well as various amounts of metamorphosed sandstones and conglomerates, and horizons of limestones and calcareous schists. Apparently only biotite-hornblende granite intrusions are found among the deposits of this layer.

Finally, the uppermost structural layer is composed of continental—primarily terrigenous—sediments with various types of sandstone predominating and also volcanic rocks lying almost horizontally upon the folded base of the two lower layers. This sedimentary-volcanic sequence, known as the Beacon series, includes deposits from the Devonian to the Triassic. Within the Beacon series, dolerite sills and dikes have undergone a considerable degree of development.

Dolerite dikes are also encountered among all the other deposits of the platform; they break through the gneisses of the lower layer at various points. Thus far no Mesozoic deposits have been found within the East Antarctic platform, although it is highly probable that there are some in the form of individual thin lenses. Cenozoic deposits are represented only by outpourings of basic effusive rocks, with leucite basalts predominating. The Quaternary deposits include glacial moraines, lake, sea, and eluvial deposits, and deposits

of material transported down mountainsides, in addition to the thick blanket of continental ice.

Our concepts of the age of the rocks constituting the upper structural layer are to some extent supported by ordinary geologic methods. The age of the metamorphic rocks and granites of the lower structural layers is uncertain. In geological reviews these are usually said to be Pre-Cambrian and, quite often, Archean.

Analogies are sometimes drawn between particular types of East Antarctic metamorphic rocks and similar Archean rocks of other continents. These analogies are on rather unsure ground, and a determination of the absolute ages of the formations being compared can be used as a supplementary criterion by which to substantiate them. There have been almost no such determinations of absolute age, apart from our preliminary publications<sup>6,8</sup> and scattered determinations by foreign authors.

In this paper we present 74 determinations of the absolute ages of East Antarctic rocks. These ages were determined by the K-Ar method applied directly to the rocks. Argon was determined with a Khlopin-Gerling instrument by the method developed by E. K. Gerling.<sup>1</sup> Its isotopic composition was determined on a type Ms2 mass spectrometer.

Potassium was determined by the dipicrylamine method.<sup>9</sup> In calculating ages, the following constants were employed:  $\lambda_K = 5.57 \times 10^{-11} \text{ yr.}^{-1}$  and  $\lambda_\beta = 4.72 \times 10^{-11} \text{ yr.}^{-1}$ .

Before proceeding to an analysis of our results, we must make the following observations. Age determinations by the K-Ar method on whole rocks rather than on individual minerals may raise doubts that are entirely justified.

It has now been established that the most reliable determinations of absolute age by the K-Ar method are obtained from micas. However, in some instances—for example, when the age of the rock is not great—the differences between the ages calculated from micas and those determined directly from the rocks themselves are small. Our studies, in this monograph and elsewhere, of the constancy of the  $\text{Ar}^{40}/\text{K}^{40}$  ratio in a large number of samples of granitoids<sup>3</sup> and metamorphic rocks<sup>4</sup> of the same age have shown that the results are quite constant for formations of the same geological age although, on the whole, the ages obtained are probably somewhat less than those of muscovites and radioactive minerals from the same rocks.

A number of determinations we have made of the age of Antarctic rocks by the K-Ar method, directly on the rocks themselves and on micas taken from them, indicate that the agreement of the results is satisfactory, with the qualification that feldspar rocks give a more recent age, as a rule, than other rocks of the same age, or micaceous rocks. Particularly large discrepancies are observed between micas and feldspars from pegmatites.

We mention all these considerations because in this case we do not have a control in the form of an age determination by other methods and must therefore judge the correctness of our data by a different means. We can therefore say that in determining age by the K-Ar method directly on granitoids or metamorphic rocks, we obtained values that are close to the true values. It is possible that our values are somewhat too low, but the maximum reduction probably does not exceed 20 to 25 per cent.



TABLE 1  
ABSOLUTE AGES OF EAST ANTARCTIC ROCKS

No.	Site of sample	Rock	K (%)	Ar (cm. <sup>3</sup> /gm. $\times 10^{-8}$ )	Age (m.y.)
Littoral west of Mirny Station					
1*	Larsemann Hills	Biotite-garnet gneiss	3.38	6.05	420
2*	Larsemann Hills	Charnockite rock	2.44	4.37	420
3†	Langnes Peninsula	Leucocratic granite (vein material of migmatites)	2.08	18.1	1525
4†	Langnes Peninsula	Pegmatite	2.02	15.1	1350
5*	Mount Brown	Biotite-pyroxene gneiss	2.63	8.4	700
6*	Gaussberg	Leucite basalt	9.56	~0.8	~20
Mirny locale					
7*	Mirny	Rocks of charnockite-mangerite series	4.44	9.2	480
8†	Sputnik Island	Biotite, hornblende granite	2.70	3.62	325
9*	Haswell Islet	Pegmatite	9.65	17.65	430
10*	Stroyteley Island (Builders')	Amphibole pegmatitic granite	2.85	5.87	475
11*	Moraine Cliff	Rocks of charnockite-mangerite series	5.48	9.68	415
12*	Moraine Cliff	Pyroxene-plagioclase schist	1.09	2.21	470
13*	Moraine Cliff	Pyroxene-plagioclase schist	2.49	4.94	460
14*	Moraine Cliff	Gray vein granite	2.28	4.44	455
Bunger Hills locale					
15†	David Island	Granite-porphry	4.28	5.86	330
16†	David Island	Pegmatoid granite	4.49	9.06	470
17†	David Island	Granite	4.76	9.35	460
18†	David Island	Granite	3.65	9.02	560
19†	David Island	Shadow migmatite	2.10	6.7	695
20	Thomson (Thomas) Island	Feldspathized biotite-garnet gneiss	3.43	8.1	535
21	Thomson (Thomas) Island	Garnet gneiss	2.95	11.31	800
22†	Smelykh Island	Leucocratic granite (vein material of migmatites)	5.35	13.5	570
23†	Smelykh Island	Rocks of the charnockite-mangerite series	3.13	9.78	700
24	Kashalot Island	Shadow polymigmatite	6.48	18.5	635
25	Charnockite Island	Aplite	4.87	12.68	585
26	Kashalot Island	Rocks of the charnockite-mangerite series	2.54	8.8	745
27†	Passeshen Cliffs	Migmatite	4.03	9.35	530
28	Obruchev Hills	Aplitic granite	2.82	6.77	545
29†	Highjump Archipelago	Feldspathized granite-gneiss	3.09	6.55	490
30†	Highjump Archipelago	Pegmatite	2.67	5.68	490
31	Harris Cliffs	Rocks of the charnockite-mangerite series	1.69	5.4	700
32†	Bunger Hills	Rocks of the charnockite-mangerite series	2.41	8.3	740
33	Bunger Hills	Migmatite	0.99	3.6	775
34	Bunger Hills	Migmatite	4.46	16.20	775
35	Bunger Hills	Migmatite	3.42	11.6	735
36	Bunger Hills	Pegmatite	4.44	15.5	750
37	Bunger Hills	Shadow migmatite	1.88	5.29	625
38	Bunger Hills	Pegmatite	5.05	14.81	650
39	Bunger Hills	Biotite-pyroxene gneiss	1.70	4.87	640



TABLE 1—*Continued*

No.	Site of sample	Rock	K (%)	Ar (cm. <sup>3</sup> /gm. × 10 <sup>-6</sup> )	Age (m.y.)
Bunger Hills locale—( <i>Continued</i> )					
40	Bunger Hills	Feldspathized gneiss	2.80	9.52	730
41	Bunger Hills	Schist	3.07	16.9	1075
42	Bunger Hills	Schist	2.71	16.8	1175
43	Bunger Hills	Biotite gneiss	1.26	7.37	1130
44	Bunger Hills	Biotite-pyroxene gneiss	1.72	8.6	1000
45	Bunger Hills	Shadow migmatite	0.70	3.73	1050
46	Bunger Hills	Biotite-pyroxene schist	5.42	27.3	1005
47†	Druzhiba Island	Rocks of the charnockite-man- gerite series	4.04	13.35	715
48†	Druzhiba Island	Migmatite	3.05	15.13	995
49†	Druzhiba Island	Pink polymigmatite	3.28	22.5	1265
50	Obruchev Island	Leucocratic granite	2.14	12.64	1135
51	Mount Stratkon	Amphibolitic granite	2.75	9.0	710
52	Mount Stratkon	Pegmatite	4.49	12.1	605
53†	Mount Stratkon	Biotite schist	4.41	21.5	980
Wilkes Land					
54†	Grisson Oasis	Leucocratic granite (vein mate- rial of migmatites)	4.21	23.12	1080
55†	Grisson Oasis	Granodiorite	3.16	11.36	765
56†	Grisson Oasis	Gneiss	0.5	1.76	755
57*	Henry Bay	Biotite-amphibolic granite	3.77	13.2	755
58*	Henry Bay	Rocks of the charnockite-man- gerite series	3.13	10.06	700
59	Pornos Bay	Pegmatoid granite	4.04	22.8	1090
George V Coast					
60*	Ainsworth Bay	Gray granite	4.15	6.05	350
61	Ainsworth Bay	Granite	3.63	7.47	745
62*	Ainsworth Bay	Granite-gneiss	3.76	7.67	475
63*	Ainsworth Bay	Biotite gneiss	2.92	5.90	470
64*	Ainsworth Bay	Biotite diorite	1.56	3.19	475
65*	Ainsworth Bay	Pink granite	2.17	7.95	780
Oates Coast					
66	Wilson Hills	Granite-gneiss	3.68	7.06	450
67	Wilson Hills	Biotite gneiss	1.72	3.52	475
68	Wilson Hills	Muscovite granite	4.00	8.20	480
69	Rennick Bay	Biotite granite	1.17	1.61	330
70	Horn Bluff	Dolerite, cutting deposits of the Beacon Series	0.43	0.23	195
71	Anyuta Cape	Dolerite, cutting deposits of the Beacon Series	0.78	0.55	175
72	Eiger Islands	Rocks of the charnockite-man- gerite series	4.34	12.0	615
73	Eiger Islands	Pegmatite	7.29	17.1	535
74	Eiger Islands	Biotite-garnet rock	5.04	14.0	620

\* Samples furnished by L. V. Klimov, Institute of Arctic Geology.

† Samples furnished by P. S. Voronov. Other samples from collection of M. G. Ravich, Institute of Arctic Geology.

‡ Samples furnished by D. S. Solov'yev, Institute of Arctic Geology.

Having made these preliminary remarks, we proceed to an examination of the results (TABLE 1).

FIGURE 1 is a diagrammatic map indicating the regions examined and the most typical ages of the rocks.

According to our determinations, the oldest rocks in the Antarctic are the leucocratic granites of the Langnes Peninsula, 1525 million years (m.y.).

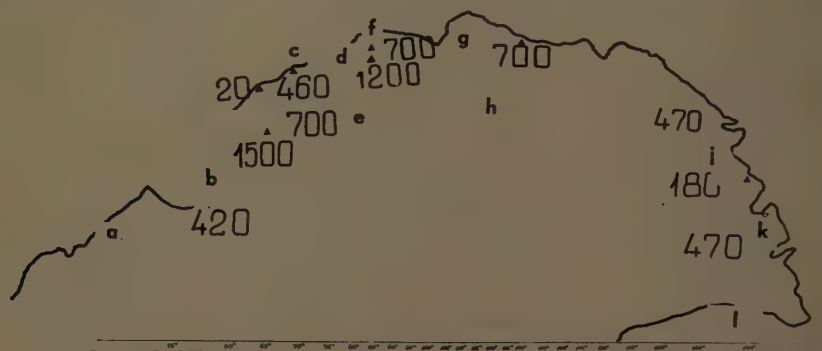


FIGURE 1. East Antarctica: (a) Mawson, (b) Ingrid Christensen Coast, (c) Mirny Station, (d) Queen Mary Coast, (e) Pionerskaya, (f) Oasis, (g) Wilkes, (h) Wilkes Land, (i) Vostok, (j) George V Coast, (k) Oates Coast, (l) Ross Sea.

TABLE 2  
ABSOLUTE AGES OF EAST ANTARCTIC ROCKS IN VARIOUS AGE GROUPS

Group No.	Groups and types of rocks	Mean age of group (m.y.)
1	Tertiary	20
2	Mesozoic	185
3	Middle Paleozoic	335
4	Lower Paleozoic	460
5	Upper Proterozoic	585
6	Middle Proterozoic	735
7	Lower Proterozoic*	1090
8	Upper Archean*	1440

\* The differentiation of the Proterozoic from the Archean group is highly arbitrary and conforms to older concepts. Current data indicate that ages in the interval 600 to 1000 m.y. should be classed as Rhiphean. The entire Pre-Cambrian scale will thus be shifted, but this usage has not yet been adopted officially.

After these come rocks of a very different age, most of which fall within the Proterozoic.

In TABLE 1 the samples examined are arranged according to geographic regions from west to east. On the basis of this table it is possible to determine the ages of rocks in various regions of the Antarctic littoral, but it is hard to establish an orderly system for classifying these rocks on an age basis.

In TABLE 2 the data are grouped according to age. With this type of arrangement, the ages of the rocks clearly fall into eight different groups.

It must be said that this classification of the rocks of East Antarctica is as

yet somewhat arbitrary. It permits a tentative orientation with respect to the age and classification of the rocks of the Antarctic Pre-Cambrian. Of course the various age groups are differentiated with various degrees of confidence. In this connection certain points ought to be made.

The few determinations of the age of Tertiary basalts and Mesozoic dolerites are in agreement with geologic concepts and do not give rise to any particular doubt.

The Middle Paleozoic group of granites is defined on the basis of only four scattered determinations but is permissible on geological grounds.

Group 4, the Lower Paleozoic group, is based on a rather large amount of material from various regions of the littoral. The largest number of samples in this group was taken in the vicinity of the Mirny Station. The scatter of age values among individual samples, among both granites and metamorphic rocks, is small and falls within the usual limits for K-Ar determinations on rocks of uniform age. It is noteworthy that there is complete agreement between the average ages of the granites and the metamorphic rocks (460 m.y.). For metamorphic rocks of course we determine not the age of deposition, as in the case of sedimentary formations, but the time of metamorphism (recrystallization);<sup>4</sup> we may therefore conclude that the Lower Paleozoic tectonic cycle was accompanied by rather considerable regional metamorphism, which brought about the recrystallization of rocks of individual zones. It should be mentioned that under East Antarctic conditions, where the amount of exposure is small and the tectonics are complex, a clear-cut delineation of individual tectonic zones in space is difficult.

We distinguish three age groups in the Proterozoic (Rhiphean). The Upper Archean (Proterozoic) group is differentiated rather arbitrarily, being based on only two age determinations. In this instance there may be significant changes later.

As we have already pointed out, the greatest age thus far—1525 m.y.—is that of the leucocratic granites (vein material of migmatites) of the Langnes Peninsula. This is certainly not a maximum age for Antarctic rocks and, in the future, we shall probably find individual rock types of still greater age.

We may conclude, from the data at our disposal thus far that the most extensively distributed rocks in East Antarctica are Proterozoic (Rhiphean) rocks.

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## Part VIII. Synthesis of Crustal History and Pre-Cambrian Time Scale

### CRUSTAL HISTORY AND THE PRE-CAMBRIAN TIME SCALE

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Many bodies of data are examined in this monograph; the complexity of this data is evident, and the difficulties of resolving events is very great.

The crustal history of the earth is complex, and our understanding of the mechanisms of both tectonism of the emplacement and mobilization of rocks is poor. Nevertheless, since the ultimate goal of the science is an understanding of crustal history, it is important to speculate and consider various ideas that treat of these processes.

Considering the various ideas that are current and have been current, it would hardly seem that my personal ignorance of this field should disqualify me from speculating, and I shall proceed to do so.

We have had in the past a sort of pre-Paleozoic myopia due to our inability to correlate Pre-Cambrian events on a continental and intercontinental scale. This myopia is evident in both the old and the new editions of a classic text on North American historical geology. The length of each chapter is roughly a monotonic decreasing function of age and, from new information now available, it does not appear that we can do much better.

Another question that is very important, and this refers to an unfortunate word used earlier, is the use of the word Pre-Cambrian. I do not think I know precisely what the word means, and I wish we could discard it. It would be better if we called it pre-olenellus or used the prefix "pre" in conjunction with some explicit time line rather than Pre-Cambrian because the base of the Cambrian is poorly defined in its present usage. A major unconformity at the base of the Cambrian in a good fossil section in one locality may have absolutely no meaning in any other place in the world.

There are a large number of very fundamental problems, and I cannot deal with them in any profound way, but I shall mention a few ideas regarding some of them. One is the question of the quantization of geological events. That is, whether the periods of tectonism and mobilization represent discrete pulses that are discrete locally or, much more, whether they are discrete on a continental or world-wide scale.

This is a very difficult question to answer now. When events are very close together, we can imagine either that they are continuous or that they are discrete. The evidence is very suggestive that there are profound events manifested on a world-wide scale; one billion-year-old events surely are characteristic in the "Grenville metamorphic episodes" in North America.

These events are present in other places in the world. The "2600 event" looks very real; but do the 2700, 2500, and 2100 dates represent different events, or is this just a smearing effect? This is very difficult to say, and at present I do not think that the data have answered this question.

Ideas of continental evolution and the question of continental accretion



have been bandied about in the trade of tectonism for a long time. The question of the existence and nature of primary and multiple secondary continental nuclei still remains obscure; the more one thinks of these ideas, the more one realizes that we have not formulated our questions so carefully that they can in fact be answered.

From this point of view, it is of first importance to define adequately continental crust in terms not of secondary but of fundamental and deep-seated characteristics. A review of the literature quickly indicates that this is rather difficult to do. An obvious and important difference between continental and oceanic land masses is that the continental land masses tend to be a discrete distance above sea level and the oceanic crust a discrete distance below sea level. This point has been emphasized by T. J. Wilson elsewhere in this monograph. It is not, however, of a sufficiently deep-seated character to provide a basic definition of these crustal masses. In the seismic literature, the definition of continental and oceanic crust is clearly defined; the continental crust has rather characteristic elastic properties and a depth to the Mohorovicic discontinuity of approximately 35 km. The oceanic crustal segments have a somewhat different seismic character and are only about 7 km. thick. This distinction is in many cases clear; however, it is again not evident that these differences are so sufficiently fundamental in character that they may be used as a definition in tectonic problems.

There are obvious petrologic differences between these crustal types. As every schoolboy knows, the continents are acidic and the oceanic rocks that we find are basic. There are of course exceptions to this rule, but at present the distinction appears to be quite real. From petrologic observations and age determinations it can be said that the acidic character of continental rocks is typical for times of about  $3 \times 10^9$  years. Whether the continents are becoming more basic or more acidic through time is a related problem that possibly may now be attacked, but at present no satisfactory data are available.

On the other hand, we can say almost nothing from this point of view about the oceanic rocks, since the only samples we have are very young. We cannot therefore say that the present apparent petrologic differences are true for any significant segment of geological time.

The petrologic differences are of great importance because they mean chemical differences. If the difference between crustal types is chemical, it implies that any change in amount and occurrence of these masses must involve macroscopic matter transport and not simply a change in pressure and temperature.

Wilson and others have pointed out that elevated land masses are intrinsically unstable due to erosional processes. Dole and Stabler have estimated that a thickness of from 20 to 40 km. is transported to the oceans and exterior (?) basins in about one eon. Using another sort of terminology this is a mean life of about 0.5 eons or less for uplifted continental masses.

In addition we know that there are about  $4.5 \times 10^9$  cu. km. of continental crustal rocks. With a uniform rate of formation over the past 4.5 eons, this means a rate of 1 cu. km. per year. This is slower than the present rate of intrusion and volcanism. It again indicates that the crustal rocks do not have any intrinsic long-term stability.

We must now ask to what extent the continents exhibit stability. The work of Ewing's group at Lamont Observatory, Palisades, N.Y., on the low velocity layer indicates that this layer is shallow under the oceanic crust and deep under the continental crust. Assuming that this effect is due to thermal softening, this could mean a thermal relaxation time of as much as a few hundred million years (m.y.).

From direct stratigraphic evidence, we know that the present continents have formed coherent units for at least 0.5 eons. While we may conclude that these structures persist over such periods of time, we may not say that they are static.

We have seen considerable age data from shield areas indicating that they now contain rocks older than 2.6 eons and in some cases 3.4 eons. These shield areas are considered to be the cores of continental masses. The usual definition of a shield area is an old land mass of low relief that has been stabilized over a long period of time. The long-time period really refers to times greater than 0.5 eons. It has been pointed out by some workers that the midcontinent of North America, if denuded, would be a perfectly good shield. There are similar examples on other continents. Such areas, if denuded, would indicate a rather stable history for more than one eon.

It is thus tempting to consider whether the stability of shields is an intrinsic character of the present shield areas and continental masses or simply a reflection of the average time constant for tectonic processes. We may ask: How sacrosanct is a shield? It is evident in many instances that continental borders are often the loci of great igneous and tectonic activity; in spite of any remarks that I may now make, I surely think that this is a fundamental tectonic character. Nevertheless, in the deep interior of continents there is evidence of considerable tectonic activity in the Rockies in North America, the Himalayas in Asia, the Urals in Eurasia, and in many other examples. These events are all rather young and, to some extent, they differ in character from the events on continental margins where there is evidence of much greater mobilization and igneous activity. These are, however, major tectonic events in the interior of stable continents. The shield areas and "possible" shield areas have all suffered repeated or multiple events. Elsewhere in this monograph there is a large number of data indicating this. The data from Michigan and Wisconsin presented by L. T. Aldrich and M. Bass are clear examples that relatively ancient areas have suffered many cycles of metamorphism. The Wichita Mountains of Oklahoma are a rather clear-cut case of instability at 0.5 eons on the continental interior of pre-existing material of 1.4 eon age as represented by the rocks in the Arbuckle Mountains.

On some continental margins there are relatively ancient terranes. For example, in Fennoscandia, Australia, North America, and Africa we have acidic rocks 1.0, 1.7, and 2.5 eons old. The presence of these rocks indicates that the continental margins need not be a locus of accretion. This does not mean that accretion does not occur. It means, in terms of simple processes, that many continental margins are not places of accretion for these time periods.

From the work of G. R. Tilton and G. W. Wetherill, elsewhere in this monograph, we see again in the eastern United States the reactivation of older pre-

existing material 1.6 eons in age between 440 to 300 m.y. At 0.5 eon ago, this might have been considered a possibly stable area. Part of this region may not be thought of as accreting in the last eon. The work of Wetherill and G. W. Gast on the gneiss domes of Fennoscandia also show *in situ* remobilization of an older basement. The primary arc on the west coast of the United States shows that in places it has been active but nonaccreting for at least 1.7 eons.

Because of the expanded time scale, there may have been active accretion in these places during earlier times. It is very reasonable to expect that the continents and ocean basins have undergone an evolution. In terms of the last 2-eon period, some of the evidence points to active but stabilized continents. I emphasize the point made by J. T. Wilson elsewhere in these pages that some sort of accretion or replenishment mechanism must exist in light of the degradational processes that are active. There is the possibility that the continental masses have retained their identity for a long part of geological time by a recycling mechanism that would involve replenishment of material without a fundamental change in their nature. It is simple to imagine such processes. From the latter point of view the question of intrinsic stability is changed to a consideration of the nature of the recycling and rejuvenation processes and their time constants.

Now there presumably are precise natural laws that must govern these processes, but from the point of view of simplicity it is interesting to speculate about the consequences of some simple probabilistic models of rejuvenation.

From some of the data presented in this monograph it is evident that many groups of data do not point to a unique time event but verge on recording continuous events. To some extent this may be a real effect if the duration of deep-seated tectonic processes and "cooling-off" times are long compared with experimental accuracy.

From this point of view, I propose to consider the stochastic problem of a unique event upon which are superimposed random events and, in the limit, the case of possible steady-state age-distribution functions.

Let us consider an assembly of rocks of various ages, each of which contains a "clock." We define  $N(x, \tau)dx$  to be the number of clocks registering a time between  $x$  and  $x + dx$  at time  $\tau$ . It is of interest to discuss this density function for certain simple phenomenological models of metamorphism and degradation in which the clock contained in each rock is reset by some mechanism to a different value than if it ran uninterruptedly starting from some initial setting. (By appropriate normalization we may consider  $N(x, \tau)dx$  to be the probability of finding a clock reading  $x$  at time  $\tau$ .) When the clocks are a radioactive parent-daughter system it is clear that a given loss or gain in the relative amounts contained in a mineral will not affect the apparent age proportionally because of the nonlinear relationship between time and parent-daughter. For the present we shall ignore this complication and assume for the sake of simplicity that the "clocks" are directly reset to some new time reading, independent of what detailed process this must entail in the material balance of the radioactive series.

If there are no processes affecting the clocks, then  $N(x, \tau + d\tau) = N(x - d\tau, \tau)$  since the only clocks that can appear reading  $x$  at time  $\tau + d\tau$  are those

that read  $x - d\tau$  at time  $\tau$ . Hence:

$$\frac{\partial N(x, \tau)}{\partial \tau} + \frac{\partial N(x, \tau)}{\partial x} = 0. \quad (1)$$

This implies that  $N(x, \tau)$  is a function of the argument  $x - \tau$ . If  $N_0(x) = N(x, 0)$ , it follows that  $N(x, \tau) = N_0(x - \tau)$  is the solution to 1. That is, each clock reading  $x$  at  $\tau = 0$  will read  $x + \tau$  at time  $\tau$ .

Let us now suppose that the clocks are arbitrarily reset with a constant equal probability of  $\lambda$  per clock per second. Then  $\lambda N(x, \tau) d\tau$  is the number of clocks reading  $x$  that are reset at time  $\tau$ . We assume that the total number of clocks is conserved. Thus:

$$\int_{-\infty}^{+\infty} N(x, \tau) dx = \eta \text{ (a constant).}$$

The total number of clocks reset in time  $d\tau$  is  $\lambda \eta d\tau$ .

Define  $\psi(x, x', \tau) dx$  to be the probability that, if a clock reading  $x'$  is reset, it is reset to read in the interval  $x, x + dx$ . As  $\psi$  is a probability density,

$$\int_{-\infty}^{+\infty} \psi(x, x', \tau) dx = 1.$$

From the definition of  $\psi$  and  $\lambda$ , the total number of clocks reset to read  $x$  in time  $d\tau$  is

$$dx d\lambda \int_{-\infty}^{+\infty} \psi(x, x', \tau) N(x', \tau) dx' \equiv \lambda \Psi(x, \tau) d\tau dx.$$

The number of clocks reading  $x$  at time  $\tau + d\tau$  is equal to the number of clocks reading  $x - d\tau$  at time  $\tau$  that are not reset during the interval  $d\tau$ , plus the number of clocks reset to read  $x$ .

$$N(x, \tau + d\tau) dx = N(x - d\tau, \tau) dx - \lambda d\tau N(x - d\tau, \tau) dx + \lambda \Psi(x, \tau) dx$$

$$\frac{\partial N(x, \tau)}{\partial x} + \frac{\partial N(x, \tau)}{\partial \tau} = -\lambda N(x, \tau) + \lambda \Psi(x, \tau) \quad (2)$$

for the case where  $\psi(x, x', \tau)$  is independent of  $x'$  and  $\tau$ ,  $\Psi(x, \tau) = \eta \psi(x)$  and a solution to 2 when  $N(x, 0) = N_0(x)$  is

$$N(x, \tau) = N_0(x - \tau) e^{-\lambda \tau} + \lambda \eta e^{-\lambda x} \int_{x-\tau}^x e^{\lambda \xi} \psi(\xi) d\xi.$$

If the resetting is to zero (total loss of daughter)  $\psi(x) = \delta(x)$  where  $\delta(x)$  is the Dirac delta function, we have

$$N(x, \tau) = N_0(x - \tau) e^{-\lambda \tau} + \lambda \eta e^{-\lambda x} S_0^\tau(x)$$

$$S_0^\tau(x) \text{ is the step function.}$$

$$S_0^\tau(x) = 1 \text{ } x \in (0, \tau)$$

$$0 \text{ } x \text{ outside } (0, \tau).$$

(3)



If all the clocks originally read zero at  $\tau = 0$ ,  $N_0(x) = \eta\delta(x)$  and

$$\frac{N(x, \tau)}{\eta} = \delta(x - \tau)e^{-\lambda\tau} + \lambda e^{-\lambda x} \quad 0 \leq x \leq \tau; \text{ zero elsewhere.}$$

FIGURE 1 shows the distribution at time  $\tau$  for the case  $N_0(x) = \eta\delta(x)$ ,  $\psi(x) = \delta(x)$ .

The initial distribution is translated to time  $\tau$  and diminished in amplitude by the factor  $e^{-\lambda\tau}$ . In addition there is a "steady-state" contribution of the reset clocks in the region  $0 \leq x \leq \tau$ . As  $\tau \rightarrow \infty$ ,

$$N \rightarrow N_\infty(x) = \lambda\eta e^{-\lambda x} \quad [0 \leq x]$$

$$0 \quad [x < 0].$$

Under steady-state conditions the time distribution of clocks is only a function of  $\lambda$  and  $x$ , its characteristics being dependent only on the rate of resetting. The higher frequency of "younger" clocks is not due to any acceleration in resetting but simply to the resetting to young (zero) age.

For the case of Equation 3 the probability  $P$  of finding a clock with a reading greater than, let us say,  $w$  ( $0 \leq w \leq \tau$ ) is  $P(x \geq w) = e^{-\lambda w}$ . For example, using a value for  $1/\lambda$  of one half of one eon we obtain the probability of finding a 4.5-eon event of  $10^{-4}$ .

It is of interest to consider the situation where  $\lambda = 0$  when  $\tau \geq a$  for the conditions of the previous problem. We shall then have a pulse, as illustrated below, traveling in time. There are two peaks present, a sharp one at  $x = \tau$ , and a saw-toothed peak at  $x = \tau - a$ . The peak of  $x = \tau$  is a true one representing some initially pure condition. The peak at  $\tau - a$  does not represent a single major event of resetting. Indeed, it represents the time at which resetting was halted. The peak is the result of steady (continuous) resetting to zero during the time interval  $a$ . The result of such a process is a "time band" representing the time interval in which the resetting processes were operative. If, instead of setting  $\lambda = 0$  when  $\tau \geq a$ , we set  $\lambda = \lambda'$  (constant)  $+\kappa\delta(\tau - a)$  and therefore reset a large number of the clocks to zero at  $\tau = a$ , we obtain the result illustrated in FIGURE 2. We observe that the peak at  $\tau - a$  has a tail on the high side. When a discrete sequence of strong metamorphic events are superimposed on a continuous randomly occurring resetting, then the resultant "shadow" of the previous event appears as a tail on the  $+x$  side of the next major event. These ages are erroneously high in terms of the event at  $\tau = a$ . They are, of course, low for the event at  $\tau$  and  $\tau - a$ , the true "parent" of the tail.

A more realistic resetting mechanism is a fractional "loss of age", for example, a clock reading  $x$  is reset to  $x/\beta$  ( $\beta > 1$ ), constituting a fractional loss of time of  $(\beta - 1)/\beta$ . In this case  $\psi(x, x', \tau) = \delta(x'/\beta - x)$ . Equation 2 becomes:

$$\frac{\partial N(x, \tau)}{\partial x} + \frac{\partial N(x, \tau)}{\partial \tau} = -\lambda N(x, \tau) + \lambda\beta N(\beta x, \tau)$$

$$\Psi = \beta N(\beta x, \tau) \quad (4)$$



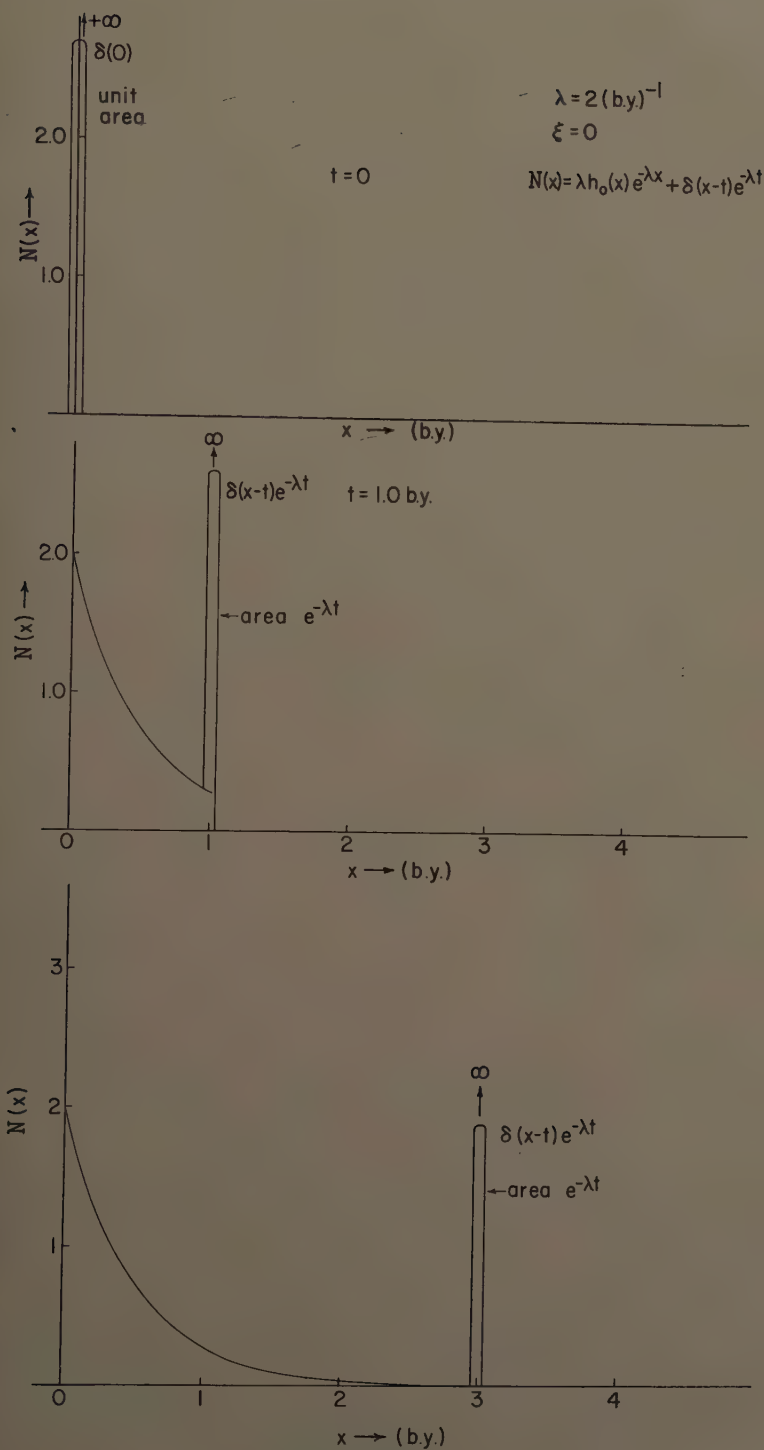


FIGURE 1.

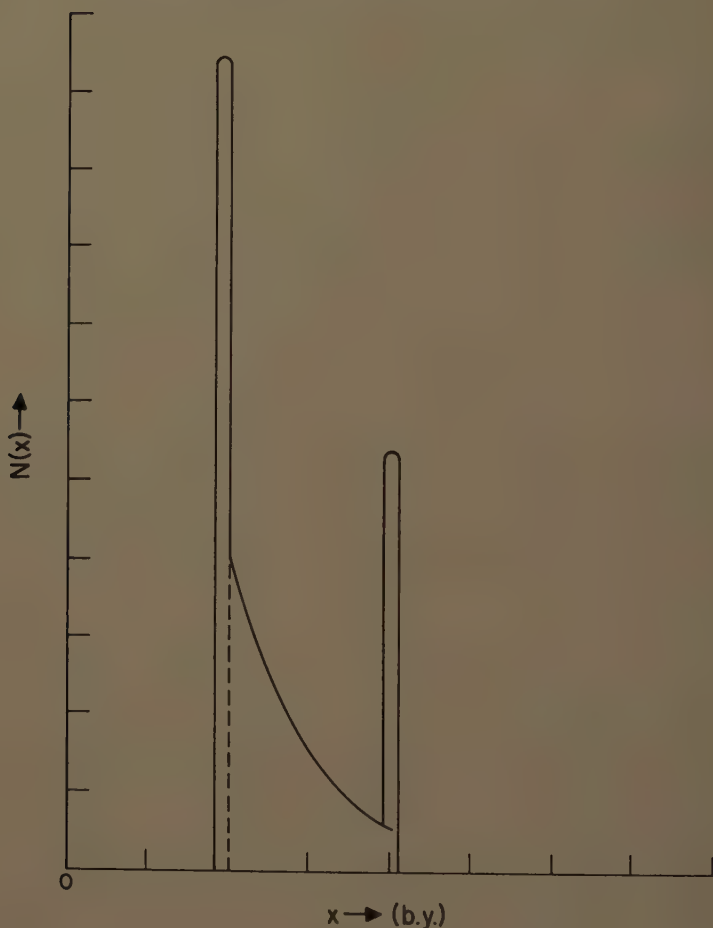


FIGURE 2.

In the steady-state case,  $\partial/\partial\tau = 0$  and 4 becomes

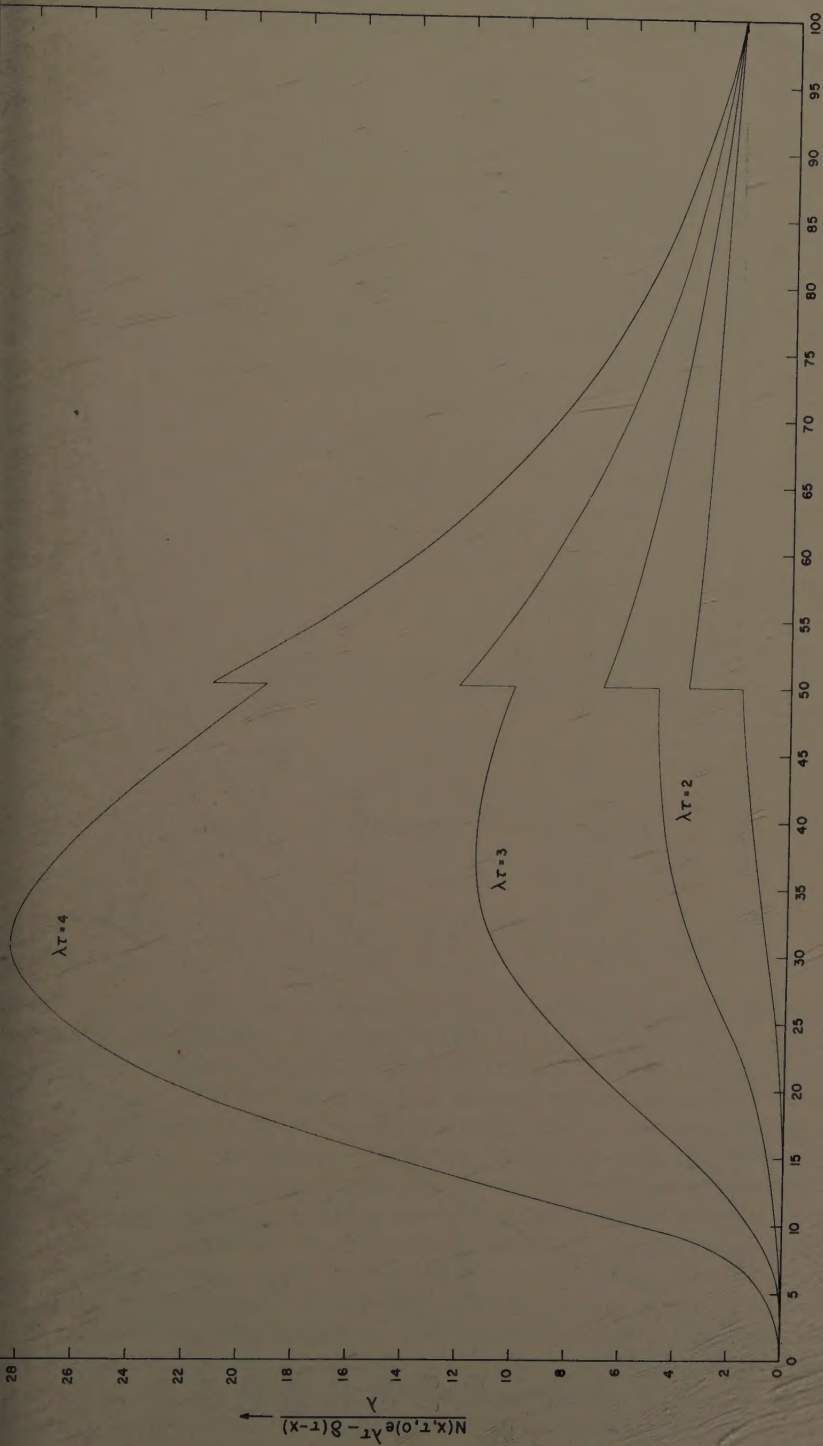
$$\frac{dN_{\infty}(x)}{dx} = -\lambda N_{\infty}(x) + \lambda\beta N_{\infty}(\beta x). \quad (5)$$

The solution to both the transient and steady-state equations has been obtained. The solution is

$$N(x, \tau, \alpha) = \delta(\tau - x + \alpha)e^{-\lambda\tau} + \sum_{n=1}^{\infty} \sum_{m=0}^n \theta_m^{n(\beta)} \frac{\lambda^n \{\tau - \beta^m x + \alpha/\beta^{n-m}\}^{n-1}}{(n-1)!} e^{-\lambda\tau} S_{\tau, m}^{\alpha, n}(x)$$

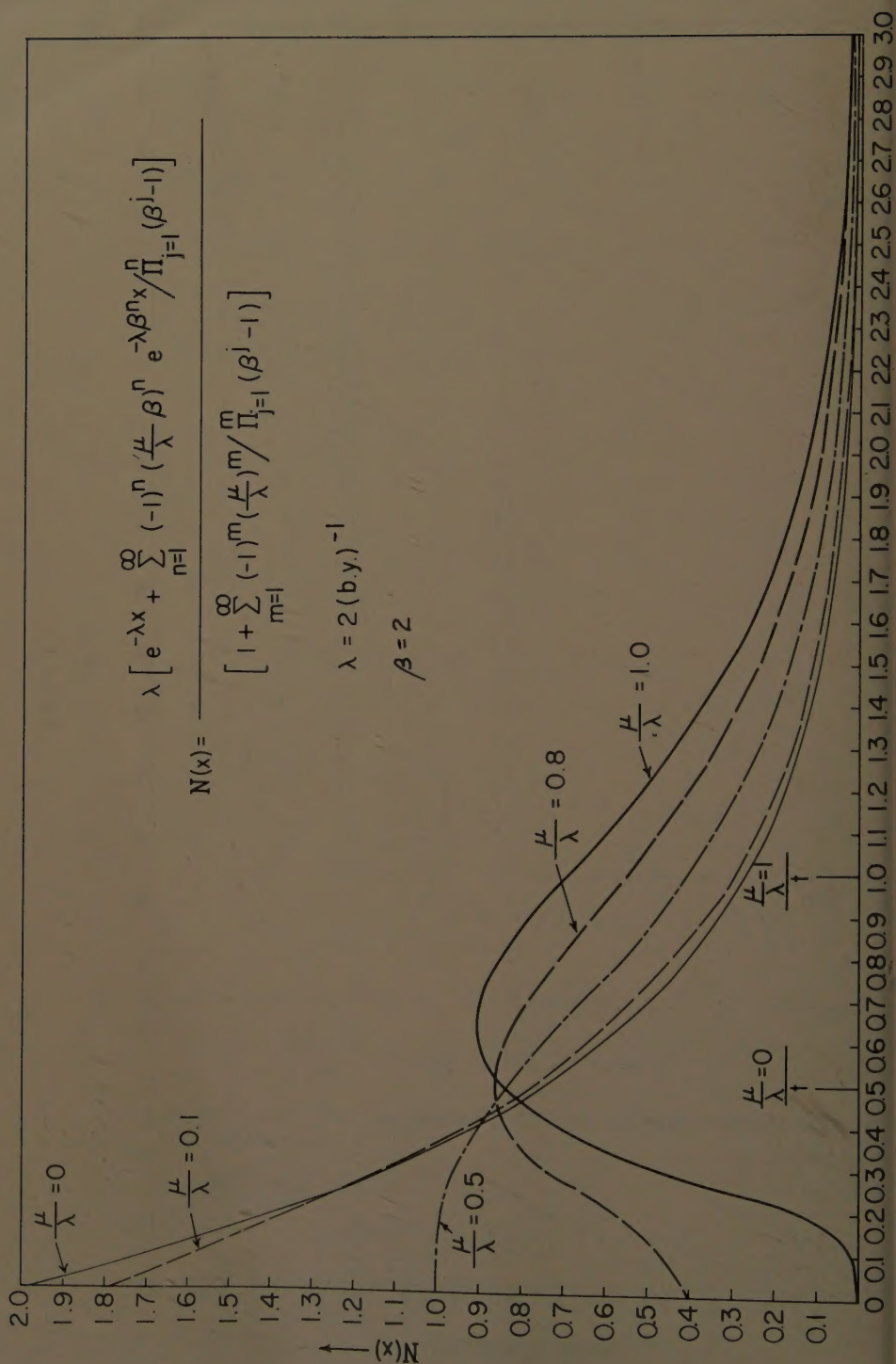
for

$$N(x, 0) = \delta(x - \alpha)$$



$\frac{\lambda x}{\lambda \tau} \rightarrow$

FIGURE 3.



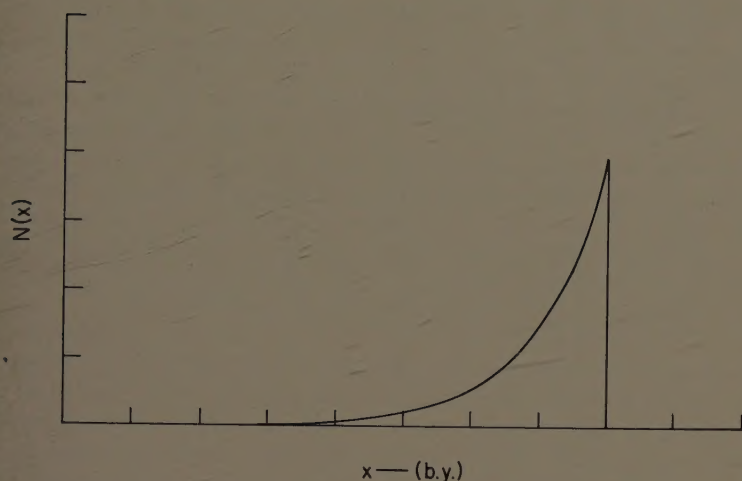


FIGURE 5.

where

$$S_{\tau,m}^{\alpha,n}(x) = 1 \quad x \in \frac{\alpha}{\beta^n} \text{ to } \frac{\alpha}{\beta^n} + \frac{\tau}{\beta^m}$$

$$0 \quad x \text{ outside}$$

and

$$\vartheta_m^n(\beta) = (-1)^m \beta^m \beta^{[(n-m+1)/2]} \pi_{n-m} \pi_m$$

and

$$\pi_i \equiv \left[ \prod_{j=1}^i (\beta^j - 1) \right]^{-1} \quad \text{and} \quad \pi_0 \equiv 1$$

This is a simple extension of the results presented by S. Chandrasekhar and G. Münch in *The Astrophysical Journal*, Vol. 114, No. 1, July 1951. The solution to the transient problem is given in FIGURE 3 for the initial condition  $N_0(x) = \delta(x)$ . It is evident for such a simple fractional time-loss mechanism that, in addition to a smearing of the distribution, a subsidiary maximum is produced at  $\tau/\beta$ . This does not represent a simple event but is simply the image of the original pure distribution due to the continuous fractional loss. This ultimately disappears into a steady-state distribution function.

FIGURE 4 illustrates the steady-state distribution for various mixtures of two resetting mechanisms: complete loss and fractional loss.

These simple stochastic models illustrate three points of particular interest.

In terms of a particular episode of mobilization with finite duration, the resulting age pattern is a time band. We must expect such effects when the duration of this period is longer than our experimental errors. The mobilization may be quite random and on a relatively fine geological scale. The con-



tinuous random resetting (to zero) of rocks of a given age produces the spectrum discussed previously. In the case of the complete mobilization of a given terrain with random withdrawal (and crystallization) of its segments, a rather similar curve is produced, the exponential "saw-tooth" being reversed, as shown in FIGURE 5. This could be expected in the case of a major deep-seated metamorphism with local decreases in intensity of metamorphism until the whole region is stabilized. In general, the actual distribution function will depend on the nature of the geologic processes; however, we should not always expect to be able to attribute a unique time to tectonic process, but rather a time band.

The second consideration is the survival problem. Geological clocks may be reset due to the recurrence of episodes of remobilization so that any event, no matter how universal, is always subject to attrition by being rejuvenated. In this way the survival chances for old events may be small, depending on the time constant for these processes. As a result, an important event may gradually "fade away" until it has a decreasingly small chance of being detected. From the apparent absence of this older event, it must not be concluded that it did not occur. We must always look for hints of preceding events by using all the methods at our disposal.

In the limiting case, a steady-state distribution of ages may be obtained; the details will of course depend on the nature of the processes. The age pattern thus produced will not be merely a complete historical evolution. It will be more a reflection of the time constant and mechanism of "resetting." This effect will be greatest in the Pre-Cambrian due to our inability to establish stratigraphic or exact absolute time lines on a large scale. The high frequency of occurrences of young rocks may not be interpreted as being caused by an increase in the rate of metamorphism, but may be simply due to a constant rate of metamorphism.

In the steady-state case objects of, let us say, 1 eon age may always be present. It is not that these objects are intrinsically stable. By the time they are rejuvenated, some other object of this age will appear. Therefore, from the point of view of probability, the question of intrinsic stability is completely changed when the time scale is much longer than the time constant for mobilization. We should thus be cautious about attributing a character of intrinsic stability to shield areas, since this may be more a reflection of the time scale of tectonic events rather than an intrinsic stability of parts of the continents in themselves.